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HANDBOOK OF METHODS FOR ACID DEPOSITION STUDIES LABORATORY ANALYSES FOR SOIL CHEMISTRY

by

Blume, L.J., B.A. Schumacher, P.W. Schaffer, K.A. Cappo, M.L. Papp,
R.D. Van Remortel, D.S. Coffey, M.G. Johnson, and D.J. Chaloud

A Contribution to the
National Acid Precipitation Assessment Program

Aquatic Effects Research Program

U.S. Environmental Protection Agency
Office of Modeling, Monitoring Systems, and Quality Assurance
Office of Ecological Processes and Effects Research
Office of Research and Development
Washington, D.C. 20460

Environmental Monitoring Systems Laboratory, Las Vegas, Nevada 89193
Environmental Research Laboratory, Corvallis, Oregon 97333

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This document is a contribution to the National Acid Precipitation Assessment Program. The methods described in this document have been developed for use in the component programs of the Aquatic Effects Research Program.

Abstract

This handbook describes methods used to process and analyze soil samples. It is intended as a guidance document for groups involved in acid deposition monitoring activities similar to those implemented by the U.S. Environmental Protection Agency's Aquatic Effects Research Program, a part of the National Acid Precipitation Assessment Program. These methods were developed for use in the Direct/Delayed Response Project, a component project of the Aquatic Effects Research Program within the Office of Ecological Processes and Effects Research. This program addresses the following issues relating to the effects of acid deposition on aquatic ecosystems:

- The extent and magnitude of past change.
- The change to be expected in the future under various deposition scenarios.
- The maximum rates of deposition below which further change is not expected.
- The rate of change or recovery of aquatic ecosystems if deposition rates are decreased.

The following chemical and physical parameters were measured during the Direct/Delayed Response Project and are described in this document.

- Percent fine gravel
- Percent medium gravel
- Bulk density-clod
- Bulk density-known volume
- Field-moist pH
- Loss-on-ignition (percent organic matter)
- Soil moisture
- Percent total sand
- Percent very coarse sand
- Percent coarse sand
- Percent medium sand
- Percent fine sand
- Percent very fine sand
- Percent total silt
- Percent coarse silt
- Percent fine silt
- Percent total clay
- pH in deionized water
- pH in 0.002 M calcium chloride
- pH in 0.01 M calcium chloride
- Cation exchange capacity (ammonium chloride saturating solution)
- Cation exchange capacity (ammonium acetate saturating solution)
- Calcium, exchangeable in ammonium acetate
- Magnesium, exchangeable in ammonium acetate
- Potassium, exchangeable in ammonium acetate
- Sodium, exchangeable in ammonium acetate
- Calcium, exchangeable in ammonium chloride
- Magnesium, exchangeable in ammonium chloride
- Potassium, exchangeable in ammonium chloride
- Sodium, exchangeable in ammonium chloride
- Aluminum, exchangeable in ammonium chloride
- Calcium, exchangeable in calcium chloride
- Magnesium, exchangeable in calcium chloride
- Potassium, exchangeable in calcium chloride
- Sodium, exchangeable in calcium chloride
- Iron, exchangeable in calcium chloride
- Aluminum, exchangeable in calcium chloride
- Exchangeable acidity in barium chloride
- Iron, extractable in pyrophosphate
- Aluminum, extractable in pyrophosphate
- Iron, extractable in acid-oxalate
- Aluminum, extractable in acid-oxalate
- Silicon, extractable in acid-oxalate
- Iron, extractable in citrate-dithionite
- Aluminum, extractable in citrate-dithionite
- Sulfate, extractable in deionized water
- Sulfate, extractable in sodium phosphate
- Sulfate, 0 mg S/L isotherm
- Sulfate, 2 mg S/L isotherm
- Sulfate, 4 mg S/L isotherm
- Sulfate, 8 mg S/L isotherm
- Sulfate, 16 mg S/L isotherm
- Sulfate, 32 mg S/L isotherm
- Total carbon
- Total nitrogen
- Total sulfur

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Glossary

I. Definitions

Accuracy--The degree of agreement of a measurement with an accepted or true value. As used here, accuracy is determined from the difference between recorded measurements and accepted true values of audit samples and calibration standards. Accuracy is generally expressed as percent bias.

Aliquot--A portion of sample treated (processed) in a specific way for a particular parameter or set of parameters.

Audit sample--A material with known characteristics which is used to determine the accuracy of the measurement system. In the Aquatic Effects Research Program (AERP) studies, natural media samples, prepared matrices, and certified (purchased) audit samples are employed.

Base saturation--The sum of exchangeable base cations divided by the cation exchange capacity; expressed as a percentage.

Batch--All samples, including routine, duplicate or replicate, blank, and audit samples, that are processed together at a single laboratory on a single day.

Bias--A systematic difference between repeated measurements and an accepted or true value.

Blank sample--Two different blank samples are referenced in these methods:

1. Calibration blank -- A 0 mg/L standard that contains only the matrix of the calibration standards. The measured concentration should be less than or equal to the contract-required detection limit.
2. Reagent blank -- A reagent blank contains all of the reagents (in the same quantities) used in preparing a regular sample for analysis. It is processed in the same manner as a regular sample. The measured concentration should be less than or equal to the contract-required detection limit.

Bulk density--The weight of dry soil per unit volume including pore space; expressed in g/cm^3.

Bulk sample--Soil samples taken from a designated portion of a specific horizon. As used here, the bulk sample is approximately 1 gallon of soil that weighs approximately 5.5 kilograms. All analyses except bulk density are performed on aliquots prepared from the bulk sample.

Calibration--Establishment of a relationship between standards of known values and the recorded output of a measurement system. As used here, a calibration range is defined as the concentration range over which acceptable results of standards are obtained.

Cation exchange capacity--A measure of the quantity of readily exchangeable cations neutralizing negative charge in the soil; expressed in milliequivalents per 100 grams of soil.

Clod sample--Fist-sized, structurally intact samples taken from a designated soil horizon and treated with a Saran:acetone solution; used to determine bulk density.

Confidence Interval--A value interval that has a designated probability of including some defined parameter of the population.

Detection limit (also instrument detection limit or IDL)--Three times the standard deviation of at least 15 nonconsecutive calibration blank or detection limit quality control check sample analyses run on at least three separate days.

Duplicate--A second, independent determination of the same sample, performed by the same analyst, at essentially the same time and under the same conditions.

Exchangeable acidity--The total hydrogen ions held on soil colloids or organic matter (reserve acidity) plus those ions present in the soil solution (active acidity); expressed in milliequivalents per 100 grams of soil.

Known volume samples--Soil samples of a specific volume taken from horizons which fail to yield satisfactory clod samples; used to determine bulk density.

Matrix spike sample--Addition of a known amount of analyte (spike) to a sample portion; used to investigate chemical and matrix interferences. The spike should be approximately equal to the endogenous level or ten times the detection limit, whichever is larger.

NBS-traceable--A material or instrument which is certified against a National Bureau of Standards primary standard.

> NOTE: The National Bureau of Standards is now the National Institute of Standards and Technology; however, NBS-traceable is still the appropriate designation for standards certified prior to the name change.

Pedon--The smallest three-dimensional body of soil that is recognizable as a soil individual. The lateral dimensions are generally considered to be 1-10 m^2 which permits the study of the nature of all horizons present in the soil.

Percent relative standard deviation (%RSD)--The standard coefficient of variation, calculated by:

$$\%RSD = \frac{s}{\bar{X}} \times 100$$

where :

s = standard deviation
$\bar{X}$ = mean of recorded measurements

pH--The negative logarithm of the activity of hydrogen ions; expressed in pH units.

Precision--The mutual agreement among individual measurements of the same property. As used here, precision is calculated from results of duplicate analyses and repetitive analyses of audit samples and quality control check solutions. Precision is generally expressed in terms of percent relative standard deviation.

Preparation laboratory--As used here, a separate facility intermediate to field activities and analytical laboratories. The primary function of the preparation laboratory is to create sample batches, incorporating quality evaluation/quality control samples in such a way as to make them unknown (blind) to the analytical laboratory analysts. Additional functions of the preparation laboratory include sample processing, performance of a limited number of sample analyses, and logistical support of field activities.

Quality assurance--The overall system used to ensure that the quality control system is performing.

Quality control--The specific procedures and checks used to provide a quality product.

Quality control check sample (QCCS)--A known sample containing the analyte of interest at a concentration in the low- to mid-calibration range. Whenever possible, the QCCS should be prepared from a source independent of that used to prepare calibration standards.

Quality evaluation samples--see Audit sample.

Standard additions--A method of analysis in which equal volumes of a sample are added to a deionized water blank and to three standards containing different known amounts of the test element. Standard additions are used when matrix or chemical interferences are present.

Standard deviation--The square root of the variance of a set of values.

II. Acronyms

AA	atomic absorption spectrometry
ACS	American Chemical Society
ADS	Acid Deposition System
ADDNET	Acid Deposition Data Network
AERP	Aquatic Effects Research Program
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
$BaCl_2$-TEA	barium chloride triethanolamine
CEC	cation exchange capacity
CHN	carbon-hydrogen-nitrogen
CPR	cardio-pulmonary resuscitation
CRDL	contract-required detection limit
DDRP	Direct/Delayed Response Project
DI	deionized
DL-QCCS	detection limit quality control check sample
EPA	U.S. Environmental Protection Agency
ES	emission spectroscopy
FIA	flow injection analyzer
IC	ion chromatography
ICP	inductively coupled plasma
ID	identification
IDL	instrument detection limit
IR	infrared
LDR	linear dynamic range
LPE	linear polyethylene
LOI	loss-on-ignition
MASS	Mid-Appalachian Soil Survey
meq	milliequivalents
mV	millivolt
NAPAP	National Acid Precipitation Assessment Program
NBS	National Bureau of Standards (now National Institute of Standards and Technology)
NCASI	National Council of Paper Industry for Air and Stream Improvement
NSWS	National Surface Water Survey
OSHA	Occupational Safety & Health Administration
%RSD	percent relative standard deviation
PVC	polyvinyl chloride
QA	quality assurance
QC	quality control
QCAS	QC audit sample

II. Acronyms *(Continued)*

QCCS	QC check sample
QE	quality evaluation
RF	radio frequency
SCS	Soil Conservation Service
SRM	standard reference material
USDA/SCS	U.S. Department of Agriculture/Soil Conservation Service
VF	volume filling
VR	volume replacement

III. Measurement Symbols

°C	degrees Centigrade
cm	centimeter, 10^{-2} m
cm^3	cubic centimeter
g	gram
hr	hour
°K	degrees Kelvin
kg	kilogram, 10^3 g
L	liter
M	molar
m	meter
meq	milliequivalent
mg	milligram
min.	minute
mL	milliliter, 10^{-3} L
mm	millimeter, 10^{-3} m
mV	millivolt, 10^{-3} volt
N	normality
nm	nanometer, 10^{-9} m
μg	microgram, 10^{-6} g
μL	microliter, 10^{-6} L
μm	micron, 10^{-6} m
μS/cm	micron Siemens per centimeter
v/v	volume to volume
w/v	weight to volume
<	less than
%	percent
±	plus or minus

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Contributors to the development of the procedures presented in this document include:

- *U.S. Environmental Protection Agency*
  L. J. Blume (Environmental Monitoring Systems Laboratory-Las Vegas)
  M. R. Church (Environmental Research Laboratory-Corvallis)

- *Lockheed Engineering and Sciences Company*
  M. H. Bartling, J. K. Bartz, G. E. Byers, R. E. Cameron, K. A. Cappo, D. J. Chaloud, W. H. Cole III, J. L. Engels, M. L. Faber, J. M. Nicholson, M. L. Papp, K. M. Peres, B. A. Schumacher, K. C. Shines, R. L. Slagle, J. E. Teberg, R. L. Tidwell, and R. D. Van Remortel

- *NSI Technology Services Corporation*
  D. S. Coffey, G. R. Holdren, M. G. Johnson, and P. W. Shaffer

- *Environmental Research Laboratory*
  L. K. Fenstermaker and C. J. Palmer

- *Oak Ridge National Laboratory*
  R. S. Turner

- *Soil Conservation Service*
  L. Juve (retired), F. M. Kaisaki, and L. Shields (retired)

- *Huffman Laboratory*
  N. Fish, R. N. Heistand, E. Huffman, and D. Raines

- *Weyerhauster Laboratories*
  K. Doxsee and T. Frost

- *Harris Laboratories*
  T. Buet and K. Shields

- *University of Nebraska at Lincoln*
  J. Den and D. Knudsen

- *University of Maine*
  I. Fernandez

Aquatic Effects Research Program documents which contributed directly to evolution of the methods and, hence, to the development of this handbook include:

Anon. 1988. *Invitation for Bid on Solicitation # W802498D1.* Internal Report. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. 454 pp.

Bartling, M. H., M. L. Papp, and R. D. Van Remortel. 1988. *Direct/Delayed Response Project: Preparation Laboratory Standard Operating Procedures for the Mid-Appalachian Soil Survey.* Internal Report. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory. Las Vegas, Nevada. 61 pp.

Cappo, K., L. J. Blume, G. A. Raab, J. K. Bartz, and J. L. Engels. 1987. *Direct/Delayed Response Project: Analytical Methods Manual for the Mid-Appalachian Soil Survey.* EPA/600/8-87/020. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. 318 pp.

Cappo, K. A., L. J. Blume, G. A. Raab, J. K. Bartz, and J. L. Engels. 1987. *Analytical Methods Manual for Direct/Delayed Response Project Soil Survey.* EPA/600/8-87/020. U.S. Environmental Protection Agency, Office of Research and Development, Las Vegas, Nevada. 318 pp.

Coffey, D. S., M. L. Papp, J. K. Bartz, R. D. Van Remortel, J. J. Lee, D. A. Lammers, M. G. Johnson, and G. R. Holdren. 1987. *Direct/Delayed Response Project: Field Operations and Quality Assurance Report for Soil Sampling and Preparation in the Northeastern U.S. Volume I: Soil Sampling.* EPA 600/4-87/030. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. 193 pp.

Coffey, D. S., J. J. Lee, J. K. Bartz, R. D. Van Remortel, M. L. Papp, and G. R. Holdren. 1987. *Direct/Delayed Response Project: Field Operations and Quality Assurance Report for Soil Sampling and Preparation in the Southern Blue Ridge Province. Volume I: Sampling.* EPA 600/4-87/041. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. 205 pp.

Haren, M. and R. D. Van Remortel. 1987. *Direct/Delayed Response Project: Field Operations and Quality Assurance Report for Soil Sampling and Preparation in the Southern Blue Ridge Province of the U.S. Volume II: Preparation.* EPA 600/4-87/041. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. 28 pp.

Papp, M. L. and R. D. Van Remortel. 1990. *Direct/Delayed Response Project: Preparation Laboratory Operations and Quality Assurance Report for the Mid-Appalachian Soil Survey.* EPA/600/4-90/017. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. 183 pp.

Papp, M. L. and R. D. Van Remortel. 1988. *Direct/Delayed Response Project: Preparation Laboratory Standard Operating Procedures for the Mid-Appalachian Soil Survey.* Internal Report. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. 61 pp.

Papp, M. L. and R. D. Van Remortel. 1987. *Direct/Delayed Response Project: Field Operations and Quality Control for Soil Sampling and Preparation in the Northeastern U.S. Volume II: Preparation.* EPA 600/4-87/030. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. 142 pp.

1.0 Introduction

1.1 Aquatic Effects Research Program Handbooks

Numerous private, state, and federal groups have initiated research projects similar to those developed as components of the Aquatic Effects Research Program (AERP). Existing AERP field and laboratory manuals and quality assurance plans were not written for an overall methods application or for general use. Developed for specific survey requirements, available operational documents do not provide general guidelines and procedures that can be adapted readily by different research groups. The AERP handbooks are designed to fill this gap. As guidance documents for groups involved in acid deposition monitoring activities, the handbooks enable researchers to avoid duplication of efforts and to make maximum use of tested methods.

1.1.1 Types of Handbooks

The AERP handbooks focus on surface water chemistry, based on documents written for the National Surface Water Survey (NSWS), and on soil chemistry, based on Direct/Delayed Research Project (DDRP) reports. The handbooks contain procedures for field operations, laboratory operations, and quality assurance (QA) criteria for water and soil monitoring activities. Surface water chemistry and soil chemistry are discussed in separate, three-volume sets.

1.1.2 Structure of Volumes

Because AERP is a dynamic program, each document is contained in a three-ring binder to facilitate the insertion of additions or modifications. Each document contains an independent Table of Contents with titles, revision numbers, and effective dates of revisions; a complete, updated Table of Contents accompanies the dissemination of each revision. The availability of each volume or revision is announced in the AERP *status*.

1.1.3 Interrelationship of Volumes

Each volume of a particular handbook set represents one aspect of an acid deposition monitoring activity. Collectively, the field, laboratory, and QA handbooks offer a comprehensive guide to surface water chemistry and soil chemistry monitoring.

1.2 Content of Laboratory Analyses Handbook

This handbook describes methods used to process and analyze soil samples. These procedures are based on methods used during the three soil surveys comprising the DDRP. Most of the methods were originally based on methodologies employed by the U.S. Department of Agriculture/Soil Conservation Service (USDA/SCS), including methods described in the *National Soils Handbook* (USDA/SCS, 1983), *Soil Survey Manual* (USDA/SCS, 1951, supplement 1962), *Field Study Program Elements to Assess the Sensitivity of Soils to Acid Deposition Induced Alterations in Forest Productivity* (Fernandez, 1983), *Procedures for Collecting Soil Samples and Methods of Analysis for Soil Surveys (USDA/SCS)*, *Methods of Soil Analysis, Part 1* (Klute, 1986) and *Part 2* (Page et al., 1982), *Soil Taxonomy* (USDA/SCS, 1975), *Keys to Soil Taxonomy* (USDA/SCS, 1988), and *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples* (USDA/SCS, 1984). These original methodologies were extensively modified to meet the particular needs of the DDRP. Modifications included specifications for sample sizes, QA and quality control (QC) samples, soil-to-solution ratios, extraction times, extraction apparatus, holding times, standard internal quality control procedures, and standard or automated equipment. These methods have been further revised based on the results of the DDRP soil surveys.

The chemical and physical parameters measured, the parameter codes used in this document, the analytical methods used, and the section in this document where they are discussed are listed in Table 1-1.

Table 1-1. Parameter Descriptions and Codes

Section	*Parameter(s)*	*Parameter Code(s)*	*Description of Parameter*
4	Percent fine gravel	RF_FG	Percent fine gravel is the portion of the bulk sample with rock fragment diameter between 2 mm and 4.75 mm determined by sieving.
	Percent medium gravel	RF_MG	Percent medium gravel is the portion of the bulk sample with rock fragment diameter between 4.75 mm and 20 mm, determined by sieving.
5	Bulk density-clod	BD_CLD	Bulk density is the weight of dry soil per unit volume, including pore space. In the clod method, the bulk density is derived by calculation using air-dry and oven-dry weights of a Saran-coated clod.
	Bulk density-known volume	BD_KV	Bulk density is the weight of dry soil per unit volume, including pore space. In the known volume method, the bulk density is derived by calculation using air-dry and oven-dry weights of volume replacement or volume filling soil sample.
6	Field-moist pH	PH_MP	pH of a field-moist sample, determined in a deionized water extract using a 1:1 mineral soil to solution ration or 1:5 organic soil to solution ratio, measured with a pH meter and combination electrode.
7	Loss-on-ignition (percent organic matter)	OM_LOI	Loss-on-ignition provides an estimate of organic matter, determined by calculation using oven-dry and ashed-weights.

(continued)

Table 1-1. (Continued)

Section	*Parameter(s)*	*Parameter Code(s)*	*Description of Parameter*
8	Soil moisture	MOIST	Air-dry soil moisture measured and expressed as a percentage on an oven-dry weight basis; mineral soils are dried at 105°C, organic soils at 60°C.
9	Percent total sand	SAND	Total sand is the portion of the sample with particle diameter between 0.05 mm and 2.0 mm, and is calculated as the summation of percentages for individual sand fractions: VCOS + COS + MS + FS + VFS.
9	Percent very coarse sand	VCOS	Very coarse sand is the sand fraction between 1.0 mm and 2.0 mm; it is determined by sieving the sand which has been separated from the silt and clay.
9	Percent coarse sand	COS	Coarse sand is the sand fraction between 0.5 mm and 1.0 mm; it is determined by sieving the sand which has been separated from the silt and clay.
9	Percent medium sand	MS	Medium sand is the sand fraction between 0.25 mm and 0.50 mm; it is determined by sieving the sand which has been separated from the silt and clay.
9	Percent fine sand	FS	Fine sand is the sand fraction between 0.10 mm and 0.25 mm; it is determined by sieving the sand which has been separated from the silt and clay.
9	Percent very fine sand	VFS	Very fine sand is the sand fraction between 0.05 mm and 0.10 mm; it is determined by sieving the sand which has been separated from the silt and clay.

(continued)

Table 1-1. (Continued)

Section	*Parameter(s)*	*Parameter Code(s)*	*Description of Parameter*
9	Percent total silt	SILT	Total silt is the portion of the sample with particle diameter between 0.002 mm and 0.05 mm; it is calculated by subtracting from 100 percent the sum of the total sand and clay.
9	Percent coarse silt	COSI	Coarse silt is the silt fraction between 0.02 mm and 0.05 mm; it is calculated by subtracting the fine silt fraction from the total silt.
9	Percent fine silt	FSI	Fine silt is the silt fraction between 0.002 mm and 0.02 mm; it is determined by pipetting and is calculated by subtracting the clay fraction from the less than 0.02-mm fraction.
	Percent total clay	CLAY	Total clay is the portion of the sample with particle diameter of less than 0.002 mm; it is determined by pipetting.
10	pH in deionized water	PH_H20	pH is determined in a deionized water extract using a 1:1 mineral soil to solution ratio or 1:5 organic soil to solution ratio; it is measured with a pH meter and combination electrode.
10	pH in 0.002 M calcium chloride	PH_002M	pH is determined in a 0.002 M calcium chloride extract using a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio; it is measured with a pH meter and combination electrode.
10	pH in 0.01 M calcium chloride	PH_01M	pH is determined in a 0.01 M calcium chloride extract using a 1:1 mineral soil to solution ratio or 1:5 organic soil to solution ratio; it is measured with a pH meter and combination electrode.

(continued)

Table 1-1. (Continued)

Section	*Parameter(s)*	*Parameter Code(s)*	*Description of Parameter*
11	Cation exchange capacity (ammonium chloride saturating solution)	CEC_CL	Cation exchange capacity, determined with an unbuffered 1 M ammonium chloride solution is the effective CEC which occurs at approximately the field pH when combined with the acidity component; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; samples are analyzed for ammonium content by one of three methods: automated distillation/titration, manual distillation/automated titration, or ammonium displacement/flow injection analysis.
11	Cation exchange capacity (ammonium acetate saturating solution)	CEC_OAC	Cation exchange capacity determined with 1 M ammonium acetate solution buffered at pH 7.0 is the theoretical estimate of the maximum potential CEC for a specific soil when combined with the acidity component; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; samples are analyzed for ammonium content by one of three methods: automated distillation/titration, manual distillation/automated titration, or ammonium displacement/flow injection analysis.
12	Calcium exchangeable in ammonium acetate	CA_OAC	Exchangeable calcium determined with 1 M ammonium acetate solution buffered at pH 7.0; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is specified.

(continued)

Table 1-1. (Continued)

Section	*Parameter(s)*	*Parameter Code(s)*	*Description of Parameter*
12	Magnesium, exchangeable in ammonium acetate	MG_OAC	Exchangeable magnesium is determined with 1 M ammonium acetate solution buffered at pH 7.0; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is specified.
12	Potassium, exchangeable in ammonium acetate	K_OAC	Exchangeable potassium is determined with 1 M ammonium acetate solution buffered at pH 7.0; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry or emission spectroscopy is specified.
12	Sodium, exchangeable in ammonium acetate	NA_OAC	Exchangeable sodium is determined with 1 M ammonium acetate solution buffered at pH 7.0; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, or emission spectrometry is specified.
13	Calcium, exchangeable in ammonium chloride	CA_CL	Exchangeable calcium is determined with an unbuffered 1 M ammonium chloride solution; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is specified.
13	Magnesium, exchangeable in ammonium chloride	MG_CL	Exchangeable magnesium is determined with an unbuffered 1 M ammonium chloride solution; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is specified.

(continued)

Table 1-1. (Continued)

Section	*Parameter(s)*	*Parameter Code(s)*	*Description of Parameter*
13	Potassium, exchangeable in ammonium chloride	K_CL	Exchangeable potassium is determined with an unbuffered 1 M ammonium chloride solution; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry or emission spectroscopy is specified.
13	Sodium, exchangeable in ammonium chloride	NA_CL	Exchangeable sodium is determined with an unbuffered 1 M ammonium chloride solution; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, or emission spectroscopy is specified.
13	Aluminum, exchangeable in ammonium chloride	AL_CL	Exchangeable aluminum is determined with an unbuffered 1 M ammonium chloride solution; approximately 1:13 mineral soil to solution ratio or 1:52 organic soil to solution ratio are used; inductively coupled plasma atomic emission spectrometry is specified.
14	Calcium, exchangeable in calcium chloride	CA_CL2	Extractable calcium is determined by a 0.002 M calcium chloride extraction; a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio are used; the calcium is used to calculate lime potential; atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is specified.
14	Magnesium, exchangeable in calcium chloride	MG_CL2	Extractable magnesium is determined by a 0.002 M calcium chloride extraction; a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio are used; atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry is specified.

(continued)

Table 1-1. (Continued)

Section	*Parameter(s)*	*Parameter Code(s)*	*Description of Parameter*
14	Potassium, exchangeable in calcium chloride	K_CL2	Extractable potassium is determined by a 0.002 M calcium chloride extraction; a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio are used; atomic absorption spectrometry or emission spectrometry is specified.
14	Sodium, exchangeable in calcium chloride	NA_CL2	Extractable sodium is determined by a 0.002 M calcium chloride extraction; a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio are used; atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, or emission spectroscopy is specified.
14	Iron, exchangeable in calcium chloride	FE_CL2	Extractable iron is determined by a 0.002 M calcium chloride extraction; a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio are used; inductively coupled plasma atomic emission spectrometry is specified.
14	Aluminum, exchangeable in calcium chloride	AL_CL2	Extractable aluminum is determined by a 0.002 M calcium chloride extraction; a 1:2 mineral soil to solution ratio or 1:10 organic soil to solution ratio are used; the aluminum concentration obtained from this procedure is used to calculate aluminum potential; inductively coupled plasma atomic emission spectrometry is specified.
15	Exchangeable acidity in barium chloride	AC_BACL	Total exchangeable acidity is determined by titration in a buffered (pH 8.2) barium chloride triethanolamine extraction using an approximately 1:30 soil to solution ratio.
16	Iron, extractable in pyrophosphate	FE_PYP	Extractable iron is determined by a 0.1 M sodium pyrophosphate extraction using a 1:100 soil to solution ratio; the pyrophosphate extract estimates organically-bound iron; inductively coupled plasma atomic emission spectrometry is specified.

(continued)

Table 1-1. (Continued)

Section	*Parameter(s)*	*Parameter Code(s)*	*Description of Parameter*
16	Aluminum, extractable in pyrophosphate	AL_PYP	Extractable aluminum is determined by a 0.1 M sodium pyrophosphate extraction using a 1:100 soil to solution ratio; the pyrophosphate extract estimates organically-bound aluminum; inductively coupled plasma atomic emission spectrometry is specified.
16	Iron, extractable in acid-oxalate	FE_AO	Extractable iron is determined by an ammonium oxalate-oxalic acid extraction using a 1:100 soil to solution ratio; the acid oxalate extract estimates organic and amorphous iron oxides; inductively coupled plasma atomic emission spectrometry is specified.
16	Aluminum, extractable in acid-oxalate	AL_AO	Extractable aluminum is determined by an ammonium oxalate-oxalic acid extraction using a 1:100 soil to solution ratio; the acid oxalate extract estimates organic and amorphous aluminum oxides; inductively coupled plasma atomic emission spectrometry is specified.
16	Silicon, extractable in acid-oxalate	SI_AO	Extractable silicon is determined by an ammonium oxalate-oxalic acid extraction using a 1:100 soil to solution ratio; inductively coupled plasma atomic emission spectrometry is specified.
16	Iron, extractable in citrate-dithionite	FE_CD	Extractable iron is determined by a sodium citrate-sodium dithionite extraction using a 1:30 soil to solution ratio; the citrate dithionite extract estimates non-silicate iron; inductively coupled plasma atomic emission spectrometry is specified.
16	Aluminum, extractable in citrate-dithionite	AL_CD	Extractable aluminum is determined by a sodium citrate-sodium dithionite extraction using a 1:30 soil to solution ratio; the citrate dithionite extract estimates non-silicate aluminum; inductively coupled plasma atomic emission spectrometry is specified.

(continued)

Table 1-1. (Continued)

Section	*Parameter(s)*	*Parameter Code(s)*	*Description of Parameter*
17	Sulfate, extractable in deionized water	SO4_H2O	Extractable sulfate is determined with a double deionized water extract; this extraction approximates the sulfate which will readily enter the soil solution and uses a 1:20 mineral soil to solution ratio or 1:40 organic soil to solution ratio; ion chromatography is specified.
17	Sulfate, extractable in sodium phosphate	SO4_PO4	Extractable sulfate is determined with a 0.016 M sodium phosphate (500 mg P/L) extract; this extraction approximates the total amount of adsorbed sulfate and uses a 1:20 mineral soil to solution ratio or 1:40 organic soil to solution ratio; ion chromatography is specified.
18	Sulfate, 0 mg S/L isotherm	SO4_0	Sulfate remaining in a 0 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio or 1:20 organic soil to solution ratio; the data are used to develop sulfate isotherms; ion chromatography is specified.
18	Sulfate, 2 mg S/L isotherm	SO4_2	Sulfate remaining in a 2 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio or 1:20 organic soil to solution ratio; the data are used to develop sulfate isotherms; ion chromatography is specified.
18	Sulfate, 4 mg S/L isotherm	SO4_4	Sulfate remaining in a 4 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio or 1:20 organic soil to solution ratio; the data are used to develop sulfate isotherms; ion chromatography is specified.

(continued)

Table 1-1. (Continued)

Section	*Parameter(s)*	*Parameter Code(s)*	*Description of Parameter*
18	Sulfate, 8 mg S/L isotherm	SO4_8	Sulfate remaining in a 8 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio or 1:20 organic soil to solution ratio; the data are used to develop sulfate isotherms; ion chromatography is specified.
18	Sulfate, 16 mg S/L isotherm	SO4_16	Sulfate remaining in a 16 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio or 1:20 organic soil to solution ratio; the data are used to develop sulfate isotherms; ion chromatography is specified.
18	Sulfate, 32 mg S/L isotherm	SO4_32	Sulfate remaining in a 32 mg S/L solution following equilibration with a 1:5 mineral soil to solution ratio or 1:20 organic soil to solution ratio; the data are used to develop sulfate isotherms; ion chromatography is specified.
19	Total carbon	C_TOT	Total carbon is determined by rapid oxidation followed by infrared detection or thermal conductivity detection using an automated CHN analyzer; total carbon can be used to characterize the soil organic matter.
19	Total nitrogen	N_TOT	Total nitrogen is determined by rapid oxidation followed by infrared detection or thermal conductivity detection using an automated CHN analyzer; total nitrogen can be used to characterize the soil organic matter.
20	Total sulfur	S_TOT	Total sulfur is determined by automated sample combustion followed by infrared detection of evolved sulfur dioxide.

1.3 Overview of the DDRP

Concern about the effects of acidic deposition on the Nation's surface water resources led the U.S. Environmental Protection Agency (EPA) to initiate research in the field in the late 1970s. Early research, focusing on a diversity of potential effects, provided insight into those research areas which were considered central to key policy questions. Recognizing the need for an integrated, stepwise approach to resolve the issues, EPA implemented the AERP in 1983 with its present structure, focus, and approach. The AERP is also a major component of the National Acid Precipitation Assessment Program's (NAPAP) Aquatic Effects Research Task Group 6, a cooperative effort of nine federal agencies tasked with addressing important policy and assessment questions relating to the acidic deposition phenomenon and its effects.

The DDRP is one of the major component projects within the AERP. Its principal mandate is to make regional projections of future effects of sulfur deposition on long-term surface water chemistry based on the best available data and most widely accepted hypotheses of the acidification process (Church et al., 1989). Regional survey boundaries for DDRP component projects are based on *Land Resource Regions and Major Land Resource Areas of the Northeast United States*. (USDA/SCS, 1985). Specific objectives of the DDRP are:

- To describe the regional variability of soil and watershed characteristics.
- To determine which soil and watershed characteristics are most strongly related to surface water chemistry.
- To estimate the relative importance of key watershed processes in moderating regional effects of acidic deposition.
- To classify a sample of watersheds with regard to their response characteristics to inputs of acidic deposition and to extrapolate the results from this sample of watersheds to the study regions.

Watershed retention of atmospherically deposited sulfur is an important consideration within the DDRP, as are the dynamics of retention via soil sulfate adsorption. Also considered are "single-factor" models (Bloom and Grigal, 1985; Reuss and Johnson 1985, 1986) of the influence of acidic deposition on the supply of base cations from soils to surface waters. The purpose of this modeling is to evaluate the potential relative importance of cation exchange as a process mediating surface water acidification. (Church et al., 1989.)

Watershed models are used in the DDRP to project future, integrated effects of atmospheric sulfur deposition on surface water chemistry. Three models specifically developed to investigate the effects of acidic deposition on watersheds and surface waters are used: (1) the Model of Acidification of Groundwater in Catchments (MAGIC) (Cosby et al., 1985a,b; 1986a,b), (2) the Enhanced Trickle Down (ETD) Model (Lee, 1987; Nikolaidis et al., 1988; Schnoor et al., 1986); and (3) the Integrated Lake-Watershed Acidification Study (ILWAS) Model (Chen et al., 1983; Gherini et al., 1985). The three models are run using common data sets for forcing functions (e.g., rainfall, runoff, atmospheric deposition) and data aggregated from the DDRP soils data base for state variables (e.g., soil physical and chemical variables). Projections of changes in annual average surface water chemistry are being made for each region for at least 50 years for two scenarios of atmospheric sulfur deposition (Church et al., 1989).

1.4 References

Bloom, P. R., and D. F. Grigal. 1985. Modeling soil response to acidic deposition in non-sulfate adsorbing soils. *J. Environ. Qual.* 14:489-495.

Chen, C. W., S. A. Gherini, J. D. Dean, R. J. M. Hudson, and R. A. Goldstein. 1983. *Modeling of Precipitation Series,* Volume 9. Ann Arbor Sciences, Butterworth Publishers, Boston, MA.

Church, M. R., K. W. Thorton, P. W. Shaffer, D. L. Stevens, B. P. Rochelle, G. R. Holdren, M. G. Johnson, J. J. Lee, R. S. Turner, D. L. Cassell, D. A. Lammers, W. G. Campbell, C. I. Liff, C. C. Brandt, L. H. Liegel, G. D. Bishop, D. C. Mortenson, S. M. Pierson and D. D. Schmoyer. 1989. *Future Effects of Long-Term Sulfur Deposition on Surface Water Chemistry in the Northeast and Southern Blue Ridge Province: Results of the Direct/Delayed Response Project.* U.S. Environmental Protection Agency, EPA/600/3-89/061, Washington, D.C.

Cosby, B. J., G. M. Hornberger, J. N. Galloway, and R. F. Wright. 1985a. Modeling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry. *Water Resour. Res.* 21:51-63.

Cosby, B. J., G. M. Hornberger, J. N. Galloway, and R. F. Wright. 1985b. Time scales of catchment acidification: A quantitative model for estimating freshwater acidification. *Environ. Sci. Technol.* 19:1144-1149.

Cosby, B. J., G. M. Hornberger, E. B. Rastetter, J. N. Galloway, and R. F. Wright. 1986a. Estimating catchment water quality response to acid deposition using mathematical models of soil ion exchange processes. *Geoderma* 38:77-95.

Cosby, B. J., G. M. Hornberger, R. F. Wright, and J. N. Galloway. 1986b. Modeling the effects of acid deposition: control of long-term sulfate dynamics by soil sulfate adsorption. *Water Resour. Res.* 22:1283-1292.

Fernandez, I. 1983. *Field Study Program Elements to Assess the Sensitivity of Soils to Acidic Deposition Induced Alterations in Forest Productivity.* National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) Technical Bulletin, No. 404.

Gherini, S. A., L. Mok, R. J. Hudson, G. F. Davis, C. W. Chen, and R. A. Goldstein. 1985. The ILWAS model: Formulation and application. *Water, Air, Soil Pollut.* 26:425-459.

Klute, A., (ed). 1986. *Methods of Soil Analysis: Part 1. Physical and Mineralogical Methods.* Agronomy Monograph No. 9, 2nd edition. American Society of Agronomy/Soil Science Society of America, Madison, Wisconsin.

Lee, S. 1987. *Uncertainty Analysis for Long-term Acidification of Lakes in Northeastern USA.* Ph.D. Thesis. University of Iowa, Iowa City.

Nikolaidis, N. P., H. Rajaram, J. L. Schnoor, and K. P. Georgakakos. 1988. A generalized soft water acidification model. *Water Resour. Res.* 24:1983-1996.

Page, A. L., R. H. Miller, and D. R. Keeney (eds.). 1982. *Methods of Soil Analysis: Part 2, Chemical and Microbiological Properties.* Agronomy Monograph No. 9, 2nd Edition. American Society of Agronomy/Soil Science Society of America, Madison, Wisconsin.

Reuss, J. O., and D. W. Johnson. 1985. Effect of soil processes on the acidification of water by acid deposition. *J. Environ. Qual.* 14:26-31.

Reuss, J. O., and D. W. Johnson. 1986. *Acid Deposition and the Acidification of Soils and Waters.* Ecological Studies Volume 59. Springer-Verlag, Inc., New York, New York.

Schnoor, J. L., N. P. Nikolaidis, and G. E. Glass. 1986. Lake resources at risk to acidic deposition in the Upper Midwest. *J. Water Pollut. Control Fed.* 58:139-148.

U.S. Department of Agriculture/Soil Conservation Service. 1951. Supplement 1962. *Soil Survey Manual.* Agriculture Handbook No. 18, U.S. Department of Agriculture, Washington, D.C.

U.S. Department of Agriculture/Soil Conservation Service. 1972. *Procedures for Collecting Soil Samples and Methods of Analysis for Soil Surveys.* Soil Survey Investigations Report No. 1, U.S. Department of Agriculture. U.S. Government Printing Office, Washington, D.C.

U.S. Department of Agriculture/Soil Conservation Service. 1975. *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Survey.* Agriculture Handbook No. 436, U.S. Department of Agriculture, U.S. Government Printing Office, Washington, D.C.

U.S. Department of Agriculture/Soil Conservation Service. 1983a. *National Soils Handbook.* Title 430, U.S. Department of Agriculture, Washington, D.C.

U.S. Department of Agriculture/Soil Conservation Service. 1984. *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples.* Soil Survey Investigations Report No. 1, USDA. U.S. Government Printing Office, Washington, D.C.

U.S. Department of Agriculture/Soil Conservation Service. 1985. *Land Resource Regions and Major Land Resource Areas of the Northeast United States (map).* U.S. Department of Agriculture, Fort Worth, Texas.

U.S. Department of Agriculture/Soil Conservation Service. 1988. *Keys to Soil Taxonomy.* Technical Monograph No. 6, U.S. Department of Agriculture/Agronomy Department, Cornell University, Ithaca, New York.

2.0 Preparation Laboratory Facilities and Organization

Large regional surveys, such as those conducted in the DDRP, result in the collection of numerous samples. Analysis should be efficient and prompt to permit resampling to be conducted, if necessary to replace lost or destroyed samples. Such surveys may require the use of multiple analytical laboratories. In such cases, a preparation laboratory may be a desirable option.

The preparation laboratory is designed to be the link between the sampling crews and the analytical laboratories. The primary functions of the preparation laboratory are to prepare homogeneous subsamples from processed bulk samples and to transfer batches of those subsamples to the analytical laboratories. For these tasks to be successfully accomplished, the preparation laboratory must uniformly track, process, and store all samples.

The preparation laboratory staff may also perform certain soil analyses. These include the determinations of percent air-dry moisture, percent rock fragments in the 2- to 20-mm fractions, percent organic matter content by loss-on-ignition, field-moist pH in water, and bulk density.

2.1 Facilities Requirements

The soil preparation and preliminary analyses should be performed in a secure, dust-free, climate-controlled area. Fume hoods and exhaust fans must be operable for certain stages of sample processing and for the preparation of the Saran:acetone solution. A source of filtered, compressed air must be available for routine cleaning of equipment. Deionized water is required in the preparation laboratory for various analyses and cleaning. Cold storage facilities must be readily accessible with ample space to store bulk samples. Additionally, the hardware and supplies listed in Table 2-1 are required for the soil processing and analysis procedures.

Table 2-1. Preparation Laboratory Supplies

- Log books
- Raw data forms
- Munsell color book
- Pens, indelible black ink
- Kraft paper, 36" wide rolls
- Plastic gloves (unpowdered)
- Dust masks
- One-gallon paint cans
- Aluminum weighing tins
- Nalgene bottles: 2-L, 500-mL, 125-mL
- Carboys, 13-gallon capacity
- Crucibles, tolerance to 450 °C
- Evaporating dishes, tolerance to 450 °C
- Beakers, 1000-mL
- Tongs
- Ring stand
- Thermometers, 0 to 100 °C range
- Sample drying tables, PVC / nylon mesh
- Rolling pins, wooden
- Rubber stoppers, No. 10 size
- Brass sieves, square-holed: 2-mm and 4.75-mm
- Riffle splitter, Jones-type, closed-bin, with 1.25-cm baffles
- Analytical balance, accurate to 0.01 g, capacity to 500 g
- Open-pan balance, accurate to 0.1 g, capacity to 5 kg
- Balance calibration weights, 3 to 5 weights bracketing expected range
- pH meter, with proper electrodes
- Desiccators
- Desiccant
- Hot plate
- Convection oven
- Muffle furnace
- Shipping boxes
- Packing material
- Strapping tape
- Saran powder
- Acetone
- Plastic containers: 25-mL, 50-mL

2.2 Staffing

The preparation laboratory staff consists of a laboratory manager and a number of analysts. The preparation laboratory manager should be knowledgeable of laboratory methods and procedures and should have supervisory skills. Adequate staffing should be provided to ensure a fast and efficient turnaround of samples from the field to the analytical laboratories. All personnel should be thoroughly trained to perform the protocols and procedures before the sample processing begins.

Sampling crews ship samples to the preparation laboratory by using an overnight express service. The preparation laboratory manager assumes the responsibility for maintaining the integrity of all samples at the laboratory facility. After the samples have been processed and analyzed, they are assembled in batches and shipped to designated analytical laboratories for further analyses. An important function of batch formation is to place certain quality evaluation (QE) and quality control (QC) samples in the batches without revealing their identity to the analytical laboratories. A separate function of the preparation laboratory is to distribute equipment and supplies to the sampling crews. The preparation laboratory should maintain thorough documentation of sample tracking and processing. All documentation should be available to and reviewed by quality assurance (QA) personnel during the course of the survey.

Ultimately, the laboratory manager is responsible for assigning duties according to the specific project needs. The following division of responsibilities is presented as an example.

Laboratory Manager:

- Coordinates laboratory operations and time management.
- Communicates with the QA manager and staff.
- Communicates with project management personnel.
- Oversees sample receipt and storage.
- Oversees all computer data entry and evaluation procedures.
- Oversees sample preparation and analysis activities.
- Organizes analytical samples into batches.
- Tracks all samples during processing.

Laboratory Analysts:

- Enter data into computer entry and verification system.
- Run verification programs.
- Receive and log samples at cold storage.
- Organize cold storage space.
- Track all samples during processing.
- Spread samples to air dry.
- Perform field-moist pH determinations.
- Perform loss-on-ignition determinations.
- Perform air-dry moisture determinations.
- Disaggregate and sieve bulk samples.
- Perform rock fragment determinations.
- Homogenize bulk samples with riffle splitter.
- Create appropriate analytical and archive subsamples.
- Perform bulk density determinations.
- Complete necessary information on bulk sample processing sheet.

Additional Laboratory Analysts (part-time):

- Disaggregate and sieve bulk samples.
- Perform rock fragment determinations.
- Track all equipment (both field and laboratory).
- Coordinate equipment procurement, preparation, and distribution.

2.3 Training

Recommended qualifications for preparation laboratory personnel include a knowledge of basic chemistry, laboratory experience, and a high level of work quality and precision. A college degree in one of the physical sciences is recommended, but is not absolutely necessary. The nature of preparation laboratory work demands close attention to detail and the ability to perform at a consistently high level of quality.

Laboratory training programs should include complete coverage of each procedure and hands-on practice sessions. The theory and rationale for each laboratory rule and procedure should be covered in detail. A written laboratory manual that contains detailed, step-by-step procedures is invaluable during training. A typical training schedule should include one day of orientation (including an explanation of laboratory rules and an overview of operations). Another day should be devoted to explaining each method or procedure, including general laboratory procedures (Appendix A). This training should include a lecture, an observation period, a question and answer period, and hands-on practice. At the conclusion of training, written testing is recommended with follow-up, supervised practice in any areas of weakness. Each analyst should be fully trained in all areas to provide coverage for absences and potential for rotation of duties.

Particular emphasis should be placed on avoiding sample contamination throughout training and operation. Disposable sterile gloves and lab coats should be worn when handling samples. As much as possible, all sample handling should be done inside the clean air station. Eating and smoking are forbidden inside the laboratory and all personnel should wash their hands after breaks. Personnel should not wear makeup or perfume, including men's cologne. All glassware and plastic ware should be washed in deionized water meeting American Society of Testing and Materials (ASTM) specifications for Type I reagent grade water (ASTM, 1984). When adding reagents to samples, the pipet tip should not contact the sample. Acid-washed and deionized water-washed apparatus and glassware should be stored separately and both types should be labeled clearly. Counter areas should be covered in Benchkote or kraft paper which should be changed frequently. The laboratory floors and counters should be washed and swept daily. Only water should be used for washing; no soap should be used. Additional precautions regarding contamination avoidance are described in the methods relating to sample processing.

2.4 Safety

Safety is also a primary consideration in the laboratory. In most locales, inspection and certification by the local fire department is required. Smoke detectors and class A-B fire extinguishers are recommended and may be required.

Fire escape routes should be clearly marked and each person should be aware of least two escape routes from the work area. A circuit breaker with a main switch shutoff should be easily accessible to avert electrical problems. Chemicals should be stored in approved containers and cabinets; bases and acids should be stored in separate areas. Chemical spill kits should be located in each work area. Disaster plans should be developed and included in training so that each person knows exactly what to do in the event of an accident. Copies of disaster plans should also be provided to the local fire department or emergency rescue team and may be required by local ordinance. Emergency numbers should be posted next to each telephone.

Personnel safety includes wearing proper laboratory clothing (e.g., laboratory coat, fitted safety glasses or goggles, and protective footwear). If hazardous substances are used, personnel should be fitted for half-mask respirators with organic cartridges. Personnel should be certified in cardio-pulmonary resuscitation (CPR) and first aid; local Red Cross or American Heart Association groups can provide classes for a nominal fee. A medical surveillance program, including testing before and after sample handling, is recommended if hazardous materials are used. A complete physical, including blood testing, is recommended prior to initiation of potentially hazardous laboratory activities.

2.5 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01. Standard Specifications for Reagent Water,* D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

3.0 General Laboratory Procedures

This section outlines general laboratory procedures used by the preparation and analytical laboratories. The detailed procedures for analyzing physical and chemical parameters are described in sections 4.0 through 20.0.

3.1 Sample Handling

3.1.1 Preparation Laboratory Sample Receipt and Tracking

In the DDRP, four types of soil samples are sent to the preparation laboratory. These are: (1) bulk samples (routine and duplicate), (2) field audit samples, (3) clod bulk density samples, and (4) known volume bulk density samples. Field sampling procedures are described in the field sampling manuals for the DDRP (Blume et al., 1987a, and Blume et al., 1987b); and will be detailed in the *Handbook of Methods for Acid Deposition Studies, Field Methods for Soil Chemistry.*

Bulk samples are those soil samples taken from a designated portion of a specific horizon. A bulk sample contains approximately one gallon of soil and generally weighs about 5.5 Kg. The bulk samples are deposited in large plastic bags and placed within protective outer canvas bags. Each bulk sample should arrive at the laboratory with a completed DDRP Label A (Figure 3-1) affixed to the inner plastic bag.

Field audit samples are quality evaluation (QE) samples sent by QA staff to the sampling crews for inclusion in the sampling of every third pedon by each crew. The samples are sieved, packaged, and shipped in the same manner as their associated routine samples. Each field audit sample should arrive at the laboratory with a completed DDRP Label A affixed to the inner plastic bag. Both mineral and organic horizons are sampled; for the DDRP, organic soils are defined as having 20 percent or more organic matter as determined by loss-on-ignition.

Clod samples are fist-sized, structurally intact, bulk density samples taken from designated horizons. Each clod is wrapped in a hairnet and dipped briefly in a 1:5 Saran:acetone solution to help maintain the clod structure and reduce moisture loss from the clod during transport and storage. Each clod is labeled, covered by a small plastic bag, and placed in a special clod box with dividers.

NADSS Label A

Date Sampled: D D M M M Y Y

Crew ID: ______________________

Site ID: ______________________

Sample Code: ______________________

Horizon: ______ Depth: ______-______cm

Set ID: ______________________

Figure 3-1. DDRP Label A.

Known volume bulk density samples are taken from horizons where clods are unobtainable. Two types of known volume samples, volume replacement (VR) and volume filling (VF) samples, are used in the DDRP. These bulk density samples are packaged in small, pre-labeled plastic bags in much the same manner as the bulk soil samples.

The sampling crews should make every effort to inform the preparation laboratory when samples are being shipped from the field. Bulk soil samples, bulk density samples, and field audit samples are placed in box-enclosed styrofoam coolers with two frozen gel-pacs. The corresponding field data forms (Appendix B, Figure B-1) and sample shipment forms are sealed in a plastic bag and taped to the underside of the cooler cover. The outer box of the cooler should be firmly enclosed with strapping tape. The samples are shipped directly to the preparation laboratory via overnight carrier.

Because of their fragile nature, the soil clods (one type of bulk density sample) are packed securely with vermiculite in coolers separate from the bulk soil samples. Clods are stored in a well ventilated area while awaiting shipment. When samples are shipped, the sampling crew should notify the preparation laboratory manager to ensure that personnel are available to receive the samples.

All preparation laboratory personnel should be familiar with the DDRP Label A, as it is a primary tool used in sample receipt and tracking. Entries on the sample label include the date sampled, horizon designation, depth range of the horizon sampled, crew identification (ID), site ID, sample code, and set ID. The crew ID consists of four alpha-numeric characters representing the state and the crew number assigned to each sampling crew within the state. The site ID is an assigned code which designates a specific watershed. The set ID is a five-digit code relating to each day a sampling crew samples a pedon. A range of set IDs is assigned to each crew. The laboratory personnel also should be familiar with the DDRP Label B (see Figure 3-2) used to label and track analytical samples within the batches.

The field data form (Appendix B, Figure B-1) is completed by the sampling crew at the sampling site. The form lists all field data for a particular pedon, including descriptions of landform, vegetation, soil climate, and a detailed pedon characterization. The field data form also contains codes (e.g., watershed ID, assigned by the soil sampling task leader).

An adequate tracking system must be initiated to document the transfer of all samples from the field to the preparation laboratory and, finally, to the analytical laboratory. The following describes the procedure used to track samples during DDRP:

> Before sampling begins, the soil sampling task leader provides the QA manager and preparation laboratory manager with a list of watershed identification numbers (site IDs) and pedon numbers for each pedon to be sampled. This information is entered into the computer entry and verification system at the preparation laboratory prior to sample receipt.
>
> The samples received at the laboratory are checked for coding accuracy against the field data form and sample shipment form. A sample receipt raw data form (see Appendix B, Figure B-2) must be filled out completely for all samples received and logged-in at cold storage. This information is then entered and verified in the computer entry and verification system. The information is checked against the site IDs and pedon numbers that have been entered into the program. If a particular watershed/pedon combination has previously been used (e.g., the preparation laboratory has previously received samples with that watershed/pedon number or a particular watershed/pedon number cannot be found on the ID list) the soil sampling task

NADSS Label B

Batch ID: _ _ _ _ _

Sample No: _ _

Figure 3-2. DDRP Label B.

leader and the QA manager are to be notified immediately. Samples should not undergo processing until they are verified under this procedure.

All samples are to be placed in cold storage as soon as possible after receipt. Known volume bulk density samples, once checked through the sample receipt procedure, can be placed in the drying area and allowed to air dry. Bulk soil samples and field audit samples remain in cold storage until there is sufficient space in the drying area for the samples (grouped according to set ID) to be air dried. After air drying, the samples are returned to cold storage and must remain there when not being processed.

The cold storage room must be maintained at a temperature of 4 °C. It is necessary for the temperature to be monitored either by a continuous sensor or by daily thermometer readings. Any substantial deviations in temperature (± 2 °C or more) should be recorded in a log book; affected samples should be identified according to set ID and sample code.

Samples should be organized in cold storage so that a particular sample within a given set may be easily located. Samples arrive at the laboratory in sets which must be maintained during storage, processing, and shipping. Because organic and mineral analytical samples are to be batched and shipped separately, it is advisable to keep organic samples separated from mineral samples in the cold storage area.

3.1.2 Analytical Laboratory Sample Receipt and Tracking

All samples received by the analytical laboratory should be checked in by a receiving clerk who: (1) records on the shipping form the date samples are received, (2) checks the samples to identify discrepancies with entries on the shipping form, and (3) mails copies of the completed shipping form to the appropriate addresses. If there are any discrepancies, or problems such as leakage or insufficient sample, the discrepancy should be documented and the laboratory or QA manager should be notified. The receiving clerk should retain a copy of the completed shipping form for the laboratory records. The samples are refrigerated at 4 °C until sample homogenization can be performed. Sample homogenization procedures are described in Section 4.6.3.

After the sample has been homogenized, minimal bottle movement (transport, shaking, etc.) is warranted to eliminate possible sample resegregation by particle size and density. Bottles must remain closed (capped) at all times except during aliquot removal for each analysis. Bottles may remain at room temperature while analyses are being performed. Removal of an aliquot for a given analysis should be done by a random insertion of a sampler (spatula, scoop, etc.) into the bottle.

NOTE: If bottle will not be used for aliquot extraction for more than 7 days, storage of the sample at 4 °C is required. Re-warm the sample to room temperature with the bottle closed (capped) prior to further analysis.

After all analyses have been completed and the results have been checked, the analytical samples are stored at 4 °C in the event that reanalysis is necessary.

3.2 Quality Control

Quality control (QC) is an integral part of any measurement procedure to ensure that results are reliable. A summary of internal QC procedures for each method is given in Table 3-1, and copies of all QC forms are provided in Appendix B. Details on internal QC procedures used in the DDRP are described below.

3.2.1 Instrument Detection Limits

The instrument detection limits (IDLs) must meet contract-required detection limits (CRDLs); the CRDLs used in the DDRP are listed in Table 3-2. The IDL is defined as three times the standard deviation of at least 15 nonconsecutive replicate calibration blank analyses run on a minimum of three separate days. In some analyses, such as ion chromatography, a signal may or may not be obtained for a blank analysis. If a signal is not obtained for a blank analysis, the IDL is defined as three times the standard deviation of 15 nonconsecutive replicate analyses of a standard (preferably the detection limit quality control check sample (DL-QCCS), see Section 3.2.5) with a concentration four times the actual detection limit or the CRDL, whichever is less.

3.2.2 Calibration and Standardization

Prepare all calibration standards in concentration units which bracket the expected sample concentration range without exceeding the linear range of the instrument. Establish a calibration curve for each analytical method by using a minimum of three points within the linear range. The use of at least a three-point calibration curve is required in place of the manufacturer's recommendations for the instrumentation, unless those recommendations require more than three points within the linear range. The lowest standard should not be greater than 10 times the detection limit.

Next, determine the linear dynamic range (LDR) for the initial calibration. During the analysis, if the concentration of a sample falls above the LDR, two options are available. The first option is to dilute and reanalyze the sample. In this case, the diluent should have the same matrix as the sample matrix. The second option is to calibrate two concentration ranges. Samples are first analyzed on the lower concentration range. Any samples for which the concentrations exceed the upper end of the LDR are then reanalyzed on the higher concentration range. If this latter option is performed, separate QC check samples (QCCSs) must be analyzed and reported for each range.

Table 3-1. Summary of Internal Quality Control

Parameter	Procedure	Control Limits	Corrective Action
Moisture	Laboratory Triplicate Analysis Prepare and analyze two additional subsamples of one sample in each batch.	Meet precision limits in Table 3-3.	Prepare and analyze two samples in each batch in triplicate. If not within control limits, check temperature stability of the oven and repeat triplicate analyses.
	Quality Control Audit Sample (QCAS) One QCAS of known concentration is run in each batch.	QCAS must fall within accuracy windows provided by QA manager.	Check the system for source of error and reanalyze the QCAS and associated samples.
Particle Size Analysis	Calibration and Standardization Analyze a QCCS with each group of soils.	Meets precision limits in Table 3-3.	Recalibrate balance, volumetric pipet, and thermometer. Check water bath or room temperature. Then reanalyze QCCS and samples bracketed by the affected QCCS.
	Laboratory Duplicate Analysis Prepare and analyze a second subsample of one sample in every batch.	Meets precision limits in Table 3-3.	Prepare and analyze two samples in each batch in duplicate. If either is outside the precision limits, determine the source of imprecision.
	Quality Control Audit Sample One QCAS of known concentration is run in each batch.	QCAS must fall within accuracy windows provided by QA manager.	Check the system for source of error and reanalyze the QCAS and associated samples.

(continued)

Table 3-1. Continued

Parameter	Procedure	Control Limits	Corrective Action
Soil pH	Calibration and Standardization		
	Calibrate pH meter for the range of pH expected in the soil (usually pH = 4 and pH = 7 standards). Analyze a QCCS immediately after calibration and after analyzing every 10 or fewer samples.	The value of the QCCS must be 4.00 ± 0.05 and 7.00 ± 0.05.	Recalibrate pH meter and reanalyze fresh QCCS. Check wiring, static electricity, and solution level in electrode, then reanalyze fresh QCCS. Perform electronic checkout (see section 6.4.4 or 10.4.4) Replace electrode or pH meter, then reanalyze fresh QCCS.
	Analyze one reagent blank of each suspension solution.	The value should be between pH = 4.5 and 7.5.	Determine source of contamination. Prepare new solutions for reanalysis of batch.
	Laboratory Triplicate Analysis		
	Prepare and analyze two additional subsamples of one sample in every batch.	Meets precision limits in Table 3-3.	Prepare and analyze two samples in each batch in triplicate. If either is outside the precision limits, check for contamination in the suspension solution. Prepare new solutions, reanalyze the batch.
	Quality Control Audit Sample		
	One QCAS of known concentration is run in each batch.	QCAS must fall within accuracy windows provided by QA manager.	Check the system for source of error and reanalyze the QCAS and associated samples.

(continued)

Table 3-1. (Continued)

Parameter	Procedure	Control Limits	Corrective Action
Cation Exchange Capacity (CEC)	Calibration and Standardization for Distillation/Titration Method		
	Acid for titration must be restandardized weekly.	Normality of acid should not change more than 5%.	Prepare new solution.
	Calculate instrument detection limit based upon a minimum titration, i.e., smallest possible volume, and normality of acid.	Meets detection limit in Table 3-2.	Use a more dilute titrant.
	Analyze a DL-QCCS.	Value must be within 20% of the theoretical concentration.	Identify and correct problem. Acceptable result must be obtained prior to sample analysis.
	Calibration blanks (0 mg/L standard) are run before the 1st sample, after every 10 samples, and after the last sample. Three reagent blanks (reagents carried through the analytical procedure) are analyzed per batch.	Blank should be less than CRDL in Table 3-2.	Investigate and eliminate source of contamination, then reanalyze all samples associated with the high blanks.
	QCCS must be run every 10 or fewer samples.	Measure each CEC and plot the results on a control chart. Develop 95% and 99% confidence limits. Required % RSD is 10%.	Recalibrate. Analyze a second QCCS and all samples bracketed by the affected QCCS.
	Laboratory Duplicate Analysis		
	Prepare and analyze a second subsample of one sample in each batch for each saturating solution.	Meets precision limits in Table 3-3.	Prepare and analyze two samples in each batch in duplicate. If either is outside the precision limits, check for contamination. Recalibrate the balance, sample dilutor, flow injection analyzer (FIA), or titrator. Reanalyze the batch.

(continued)

Table 3-1. (Continued)

Parameter	Procedure	Control Limits	Corrective Action
Cation Exchange Capacity (continued)	Quality Control Audit Sample		
	One QCAS of known concentration is run in each batch.	QCAS must fall within accuracy windows provided by QA manager.	Check the system for source of error and reanalyze the QCAS and associated samples.
Cations - Ca, Mg, K, Na, Fe, Al, and Si	Calibration and Standardization		
	Calibrate the spectrometer as required in the analytical method. Analyze a QCCS immediately after calibration, after every 10 or fewer samples, and after the last sample of the batch.	Calculate the QCCS value from calibration curve and plot result on a control chart. Develop the 95% and 99% confidence limits. Acceptable range is ±10%.	Recalibrate instrument. Prepare new stock and calibration standards if necessary. Analyze a second QCCS and all samples bracketed by the affected QCCS.
	Verify calibration linearity. Determine linear dynamic range.	Linearity as determined by a least-squares fit should not be less than 0.99.	Check calibration standards to see if properly prepared. Prepare new stock and calibration standards if necessary, and recalibrate. Follow instrument manufacturer's trouble-shooting procedures.
	Determine the instrument detection limits.	Meets the detection limits in Table 3-2.	Check for possible contamination. Optimize instrumentation, e.g., wavelength, burner or torch position, oxidant and fuel pressures, nebulizer flow rate, integrity or impact bead or spoiler, optical alignment.
	Analyze a DL-QCCS.	Value must be within 20% of the theoretical concentration.	Identify and correct problem. Acceptable result must be obtained prior to sample analysis.

(continued)

Table 3-1. (Continued)

Parameter	Procedure	Control Limits	Corrective Action
Cations - Ca, Mg, K, Na, Fe, Al, and Si (continued)	Calibration blanks (0 mg/L standard) are analyzed before the 1st sample, after every 10 samples, and after the last sample of each batch. Three reagent blanks (any necessary reagents carried through the analytical procedure) are run per batch.	Blanks should be less than CRDL in Table 3-2. The calcium value should fall between 76 and 84 mg/L calcium.	Investigate and eliminate source of contamination, then reanalyze all samples associated with the high blank.
	Analyze one spike per batch for all required parameters.	Spike recovery should be within 90-110% of known value.	Analyze two additional spike samples; if either recovery does not fall within 90-110% of known value, notify QA manager before reporting data.
	Analyze one spike per batch for calcium chloride extraction.	Value for calcium should be between 76 and 84 mg/L.	Prepare fresh extraction solution.
	Laboratory Duplicate Analysis		
	Analyze a second subsample of one sample in each batch for each analyte.	Meets precision limits in Table 3-3.	Prepare and analyze two samples in each batch in duplicate. If either is outside the precision limits, eliminate the source of imprecision. Reanalyze the batch.
	Quality Control Audit Sample		
	One QCAS of known concentration is run in each batch.	QCAS must fall within accuracy windows provided by QA manager.	Check the system for source of error and reanalyze the QCAS and associated samples.
Exchangeable Acidity - $BaCl_2$-TEA	Calibration and Standardization		
	The solutions used for titration must be restandardized weekly.	Normality of solution should not change more than 5%.	Prepare new solution.

(continued)

Table 3-1. (Continued)

Parameter	Procedure	Control Limits	Corrective Action
Exchangeable Acidity - $BaCl_2$-TEA (continued)	Calibration and Standardization		
	Calculate instrument detection limit, based upon a minimum titration (i.e., smallest possible volume, and normality of titrants).	Meets detection limit in Table 3-2.	Use more dilute titrants.
	Calibration blanks are analyzed before the 1st sample, after every 10 samples, and after the last sample of each batch. Three reagent blanks per batch are required.	Blanks should have concentrations between 1.3 and 1.8 meq/L.	Determine and eliminate source of variation, then reanalyze the batch.
	Laboratory Duplicate Analysis		
	Prepare and analyze a second subsample of one sample in each batch.	Meets precision limits in Table 3-3.	Prepare and analyze two samples in each batch in duplicate. If either is outside the precision limits, determine source of imprecision. Reanalyze the batch.
	Quality Control Audit Sample		
	One QCAS of known concentration is run in each batch.	QCAS must fall within accuracy windows provided by QA manager.	Check the system for source of error and reanalyze the QCAS and associated samples.
Sulfate Isotherms and Extractable Sulfate	Calibration and Standardization		
	Verify calibration linearity. Determine linear dynamic range.	Linearity as determined by a least-squares fit should not be less than 0.99.	Check calibration standards, see if properly prepared. Prepare new calibration standards, if necessary, and recalibrate. Follow instrument manufacturer's troubleshooting procedures.

(continued)

Table 3-1. (Continued)

Parameter	Procedure	Control Limits	Corrective Action
Sulfate Isotherms and Extractable Sulfate (continued)	Calibrate as required in the analytical methods. Analyze a QCCS immediately after calibration and after analysis of every 10 or fewer samples.	Calculate the QCCS value from the calibration curve and plot result on a control chart. Develop the 95% and 99% confidence limits. Acceptable range is ±5%.	Recalibrate instrument. Prepare new stock and calibration standards, if necessary. Analyze a second QCCS and all samples bracketed by the affected QCCS.
	Determine instrument detection limits.	Meets detection limits in Table 3-2.	Check for possible contamination. Optimize instrumentation.
	Analyze a DL-QCCS for both extracts and the "0" isotherm.	Value must be within 20% of the known concentration.	Identify and correct problem. Acceptable results must be obtained prior to sample analysis.
	Calibration blanks (0 mg/L standard) are analyzed before the 1st sample, after every 10 samples, and after the last sample of each batch. Three reagent blanks (necessary reagents carried through the analytical procedure) are analyzed per analytical batch.	Blanks should be less than CRDL in Table 3-2 and within 5% of the required concentration for the other isotherms.	Investigate and eliminate source of contamination, then reanalyze all samples associated with the high blank. Prepare new isotherm solutions for solutions not meeting the criteria.
	Analyze one spike sample per batch for both sulfate extracts.	Spike recovery is within 95-105% of known value.	Analyze two additional spike samples; if either recovery does not fall within 95-105% of known value, notify QA manager before reporting data.
	Spike two separate soil samples per batch with 2, 8, and 32 mg S/L.	Spike recovery is within 95-105% of known value.	Analyze two additional spike samples; if either recovery does not fall within 95-105% of known value, notify QA manager before reporting data.
	Analyze spike solution.	Values should be less than CRDL for 0*mg/L, ±3% for 2,4,8 and 16 mg S/L, and ±2% for 32 mg S/L of known concentration.	Prepare fresh extraction solution.

(continued)

Table 3-1. (Continued)

Parameter	Procedure	Control Limits	Corrective Action
Sulfate Isotherms and Extractable Sulfate (continued)			
	Resolution Check Once per analytical run (day) check resolution of the anion separator column by analyzing standards containing sulfate (1 mg S/L) and phosphate (1 mg P/L) or sulfate and nitrate. Set instrument for a nearly full-scale response on the most sensitive range used.	Resolution must exceed 60%.	Clean or replace anion separator column, then repeat calibration and resolution check. The eluent may also be adjusted as needed.
	Quality Control Audit Sample One QCAS of known concentration is run in each batch.	QCAS must fall within accuracy windows provided by QA manager.	Check the system for source of error and reanalyze the QCAS and associated samples.
	Laboratory Duplicate Analysis Prepare and analyze a second subsample of one sample in each batch.	Meets precision limits in Table 3-3.	Prepare and analyze two samples in each batch in duplicate. If either is outside the precision limits, determine source of imprecision. Reanalyze the batch.
Total C,N, and S	Calibration and Sample Analysis Calibrate and standardize combustion furnace as described in method. Analyze a QCCS immediately after calibration and after analysis of every 10 or fewer samples.	Measure analyte and plot result on a control chart. Develop the 95% and 99% confidence limits (warning and control). Precision should be within limits outlined in Table 3-3.	Determine and correct problem. Recalibrate and then analyze a second QCCS and all samples bracketed by the affected QCCS.

(continued)

Table 3-1. (Continued)

Parameter	Procedure	Control Limits	Corrective Action
Total C,N, and S (continued)	Verify calibration linearity. Determine linear dynamic range.	Linearity as determined by a least-squares fit should not be less than 0.99.	Check calibration standards to see if properly prepared. Prepare new stock and calibration standards, if necessary. Recalibrate. Follow instrument manufacturer's troubleshooting procedures.
	Determine and establish IDL before initial routine analyses. The IDL equals 3 times the standard deviation of 10 nonconsecutive blank analyses.	The IDL should be less than the CRDL in Table 3-2.	Check instrumental performance using manufacturer specifications and troubleshooting guide. Recalibrate instrument and repeat.
	Analyze one DL-QCCS per batch with concentrations 2 to 3 times the CRDL.	Measured value must be within 20% of the theoretical concentration. Plot concentration on a control chart and submit charts to the QA manager.	Identify and correct problem, obtain acceptable result before continuing sample analysis. Reanalyze all affected samples.
	Matrix Spike To one sample per batch uniformly add a standard amount of analyte at the endogenous level or 10 times the instrumental detection limit, whichever is greater.	Calculate the percent recovery. Acceptable range is 100 ± 10%.	Repeat on two additional samples. If possible, determine and eliminate the source of the interference, then repeat analyses. If either or both are outside the control limits, analyze the batch by the method of standard additions.
	Reagent Blanks Analyze one reagent blank per batch for each analyte.	The reagent blank should be less than the CRDL in Table 3-2.	Determine the source of error. Prepare new blank for reanalysis of batch.
	Calibration blanks should be analyzed before the 1st sample, after every 10 samples, and after the last sample of each batch.	Calibration blanks should be less than the CRDL in Table 3-2.	Determine the source of error and reanalyze the affected samples.

(continued)

Table 3-1. (Continued)

Parameter	Procedure	Control Limits	Corrective Action
Total C, N, and S (continued)	Laboratory Duplicate Analysis		
	Prepare and analyze a second portion of one sample in every batch for each procedure.	Precision should be within limits established in Table 3-3.	Prepare and analyze two samples in duplicate. If these fall outside the range, check for source of error. Recalibrate the instrument, then reanalyze the batch.
	Quality Control Audit Sample		
	Analyze the QCAS specified on the shipping form.	Measured concentration must fall within windows given for that sample.	Check instrument troubleshooting procedures. Recalibrate and analyze all associated samples.

Table 3-2. Contract-Required Detection Limits, Reporting Units, and Expected Ranges

Parameter	CRDL[a] (mg/L)	Calculated Reporting Unit[b]	Expected Range (Median)[c]	
			Mineral Samples	Organic Samples
MOIST	—	wt. %	0.1-2.5	1.3-6.0
SAND	—	wt. %	8.0-96.0 (59.5)	—
SILT	—	wt. %	0.7-58.2 (28.3)	—
CLAY	—	wt. %	0.0-21.0 (7.1)	—
PH_H2O	—	pH units	3.5-6.0 (5.0)	2.9-5.3 (3.9)
PH_002M	—	pH units	3.1-5.7 (4.5)	2.7-5.0 (3.5)
PH_01M	—	pH units	2.9-5.5 (4.4)	2.4-4.8 (3.2)
CEC_OAC	1.05[d]/0.0075[e]	meq/100g	0.4-36.9 (9.2)	21.8-147.5 (91.3)
CEC_CL	1.05[d]/0.0075[e]	meq/100g	0.3-17.5 (5.4)	9.6-60.2 (33.3)
AC_BACL	0.005 meq	meq/100g	0.0-48.4 (9.0)	24.6-153.2 (88.2)
CA_OAC	0.05	meq/100g	0.0-4.3 (0.17)	0.3-49.4 (6.6)
MG_OAC	0.05	meq/100g	0.0-0.9 (0.08)	0.1-7.7 (2.0)
K_OAC	0.05	meq/100g	0.0-0.2 (0.07)	0.0-1.9 (0.8)
NA_OAC	0.05	meq/100g	0.0-0.1 (0.02)	0.0-0.8 (0.2)
CA_CL	0.05	meq/100g	0.0-4.9 (0.17)	0.8-37.2 (8.8)
MG_CL	0.05	meq/100g	0.0-0.9 (0.08)	0.1-7.9 (2.1)
K_CL	0.05	meq/100g	0.0-0.2 (0.07)	0.1-1.9 (0.7)
NA_CL	0.05	meq/100g	0.0-0.1 (0.02)	0.0-0.8 (0.2)
AL_CL	0.10	meq/100g	0.0-0.5	0.0-1.0
CA_CL2	0.50	meq/100g	0.2-0.8 (0.5)	0.5-4.2 (2.2)
MG_CL2	0.05	meq/100g	0.0-0.2 (0.04)	0.0-1.4 (0.7)
K_CL2	0.05	meq/100g	0.0-0.05 (0.01)	0.0-1.0 (0.4)
NA_CL2	0.05	meq/100g	0.0-0.06 (0.02)	0.0-0.4 (0.1)
FE_CL2	0.10	meq/100g	0.0-0.04 (0.01)	0.0-0.2 (0.03)
AL_CL2	0.10	meq/100g	0.0-0.2 (0.01)	0.0-0.6 (0.2)
FE_PYP	0.50	wt. %	0.0-1.2 (0.2)	0.0-1.0 (0.2)
AL_PYP	0.50	wt. %	0.0-1.1 (0.2)	0.0-1.0 (0.2)
FE_AO	0.50	wt. %	0.0-1.7 (0.3)	0.0-1.1 (0.2)
AL_AO	0.50	wt. %	0.0-2.0 (0.3)	0.0-1.1 (0.2)
SI_AO	0.50	wt. %	0.0-2.0	0.0-1.0
FE_CD	0.50	wt. %	0.0-2.3 (1.0)	0.0-1.2 (0.3)
AL_CD	0.50	wt. %	0.0-1.3 (0.3)	0.0-0.9 (0.2)
SO4_H2O	0.025	mg S/kg	1.1-19.5 (7.6)	8.0-74.1 (44.3)
SO4_PO4	0.025	mg S/kg	0.2-87.5 (26.0)	9.8-167.3 (45.6)
SO4_0	0.025	mg S/L	0.1-3.3 (0.76)	—
SO4_2	0.025	mg S/L	0.9-4.8 (2.2)	—
SO4_4	0.025	mg S/L	1.7-6.5 (3.7)	—
SO4_8	0.025	mg S/L	3.1-10.3 (6.9)	—
SO4_16	0.025	mg S/L	6.5-17.8 (13.4)	—
SO4_32	0.025	mg S/L	15.3-33.4 (27.5)	—
C_TOT	0.010	wt. %	0.0-7.6 (0.8)	5.1-53.8 (38.0)
N_TOT	0.005	wt. %	0.0-0.4 (0.05)	0.2-2.1 (1.4)
S_TOT	0.001	wt. %	0.0-0.1 (0.01)	0.0-0.5 (0.17)

[a] Contract-required detection limit.
[b] All values determined on an oven-dry soil weight basis.
[c] Expected ranges in mg/L of reported data values for mineral and organic samples, based on the 1st, 50th, and 95th percentiles of data from previous DDRP surveys. Ranges for MOIST, AL_CL, and SI_AO parameters are anticipated.
[d] For flow injection analysis (FIA) method, in mg/L.
[e] For titration method, in meq units.

Spectroscopic-grade or high purity chemicals are recommended for primary standards when analysis is done by atomic absorption or emission methods. Also, calibration standards should have the same matrix as the solutions being analyzed.

3.2.3 Blanks

3.2.3.1 Calibration Blanks--

Analyze a calibration blank at the start of each analysis run, at specified intervals thereafter (e.g., after every ten samples), and after the last sample to check for baseline drift. The calibration blank is defined as a "0" mg/L standard and contains only the matrix of the calibration standards. The observed concentration of each calibration blank should be less than or equal to the CRDL (see Table 3-2). If it is not, rezero the instrument and recheck the calibration.

3.2.3.2 Reagent Blanks--

For methods that require exchange or extraction, prepare and analyze the recommended number (usually three) of reagent blanks for each group of samples processed. If three are run, they should be placed near the beginning, the middle, and the end of the batch. A reagent blank is composed of all reagents in the same quantities used in preparing an actual sample for analysis. The reagent blank undergoes the same digestion or extraction procedures as an actual sample. The concentration of each reagent blank should be less than or equal to the CRDL. If the concentration exceeds this limit, the source of contamination should be investigated and eliminated. A new reagent blank is then prepared and analyzed, and the same criteria are applied. All samples associated with the "high" blank should be reprocessed and reanalyzed after the contamination has been eliminated.

3.2.4 Replicate Sample Analysis

Prepare and analyze a soil sample from each batch in duplicate for each parameter; log all information on the appropriate QC form. (Some procedures recommend triplicate analysis. Refer to the specific method sections for guidance.)

For values above the cutoff level in Table 3-3, calculate the standard coefficient of variation or percent relative standard deviation (%RSD) as follows:

$$\%RSD = (s/\bar{x}) \times 100$$

where s is the standard deviation calculated for (n-1) degrees of freedom and $\bar{x}$ is the mean of the replicate samples. For values below the cutoff, calculate the standard deviation. The %RSD and standard deviation should be plotted on control charts.

If the duplicate values fall outside the precision limits outlined in Table 3-3, an explanation should be sought (e.g., instrument malfunction or calibration drift). A second sample in the batch should then be prepared and analyzed in duplicate. No additional samples should be analyzed until all duplicate sample results are within the control limits.

Table 3-3. Intralaboratory Precision Goals for Laboratory Replicates

	Precision Limits[a]					
	Mineral Samples			Organic Samples		
Parameter	Cutoff	Lower(SD)	Upper(RSD)	Cutoff	Lower(SD)	Upper(RSD)
MOIST	12.0	0.3 wt %	2.5%	12.0	0.3 wt %	2.5%
SAND	—	3.0 wt %	—	---	---	---
SILT	—	3.0 wt %	—	---	---	---
CLAY	—	2.0 wt %	—	---	---	---
PH_H2O	—	0.10 unit	—	—	0.10 unit	---
PH_002M	—	0.10 unit	—	—	0.10 unit	---
PH_01M	—	0.10 unit	—	—	0.10 unit	---
CEC_OAC	2.5	0.25 meq/100g	10%	2.5	0.25 meq/100g	10%
CEC_CL	2.5	0.25 meq/100g	10%	2.5	0.25 meq/100g	10%
AC_BACL	6.7	1.0 meq/100g	15%	6.7	1.0 meq/100g	15%
CA_OAC	0.2	0.02 meq/100g	10%	1.0	0.1 meq/100g	10%
MG_OAC	0.2	0.02 meq/100g	10%	1.0	0.1 meq/100g	10%
K_OAC	0.2	0.02 meq/100g	10%	1.0	0.1 meq/100g	10%
NA_OAC	0.2	0.02 meq/100g	10%	1.0	0.1 meq/100g	10%
CA_CL	0.2	0.02 meq/100g	10%	1.0	0.1 meq/100g	10%
MG_CL	0.2	0.02 meq/100g	10%	1.0	0.1 meq/100g	10%
K_CL	0.2	0.02 meq/100g	10%	1.0	0.1 meq/100g	10%
NA_CL	0.2	0.02 meq/100g	10%	1.0	0.1 meq/100g	10%
AL_CL	1.3	0.2 meq/100g	15%	3.3	0.5 meq/100g	15%
CA_CL2	1.0	0.05 meq/100g	5%	4.0	0.2 meq/100g	5%
MG_CL2	0.05	0.005 meq/100g	10%	0.5	0.05 meq/100g	10%
K_CL2	0.05	0.005 meq/100g	10%	0.25	0.025 meq/100g	10%
NA_CL2	0.05	0.005 meq/100g	10%	0.25	0.025 meq/100g	10%
FE_CL2	0.07	0.01 meq/100g	15%	0.33	0.05 meq/100g	15%
AL_CL2	0.33	0.05 meq/100g	15%	1.3	0.2 meq/100g	15%
FE_PYP	0.3	0.03 wt %	10%	0.3	0.03 wt %	10%
AL_PYP	0.3	0.03 wt %	10%	0.3	0.03 wt %	10%
FE_AO	0.3	0.03 wt %	10%	0.3	0.03 wt %	10%
AL_AO	0.3	0.03 wt %	10%	0.3	0.03 wt %	10%
SI_AO	0.3	0.03 wt %	10%	0.3	0.03 wt %	10%
FE_CD	0.3	0.03 wt %	10%	0.3	0.03 wt %	10%
AL_CD	0.3	0.03 wt %	10%	0.3	0.03 wt %	10%
SO4_H2O	15.0	1.5 mg S/kg	10%	15.0	1.5 mg S/kg	10%
SO4_PO4	15.0	1.5 mg S/kg	10%	15.0	1.5 mg S/kg	10%
SO4_0	2.0	0.1 mg S/L	5%	----	----	----
SO4_2	2.0	0.1 mg S/L	5%	----	----	----
SO4_4	2.0	0.1 mg S/L	5%	----	----	----
SO4_8	2.0	0.1 mg S/L	5%	----	----	----
SO4_16	2.0	0.1 mg S/L	5%	----	----	----
SO4_32	2.0	0.1 mg S/L	5%	----	----	----
C_TOT	0.05	0.05 wt. %	10%	0.5	0.05 wt. %	10%
N_TOT	0.15	0.015 wt. %	10%	0.15	0.015 wt. %	10%
S_TOT	0.02	0.002 wt. %	10%	0.02	0.002 wt. %	10%

[a] Precision objectives based on a concentration cutoff value, where the standard deviation is used for lower concentrations and the percent relative standard deviation is used for higher concentrations.

3.2.5 Quality Control Standards

Two QC standards are recommended. A detection limit QC check sample (DL-QCCS) is used to assess the validity of data near the detection limit. A QCCS is used to assess the validity of data in the mid-calibration range. Control charts must be kept for the QCCS.

DL-QCCS Standards--Analyze one DL-QCCS per batch. This is a low-level QC standard that contains the analyte of interest at a concentration two to three times above the CRDL. Log in all information on the appropriate QC form. The purpose of the DL-QCCS is to eliminate the necessity of formally determining the IDL at frequencies less than every 30 days or on a per batch basis.

QCCS Standards--Immediately after standardization of an instrument, analyze a QCCS containing the analyte of interest at a concentration in the mid-calibration range. Log in all information on the appropriate QC form. QCCS standards may be obtained commercially or may be prepared by the analyst from a source which is independent of the calibration standards. The QCCS is analyzed to verify the calibration curve prior to any sample analysis, after every 10 samples, and after the last sample in the batch.

Establish warning and control limits (i.e., the 95 and 99 percent confidence intervals). A value outside the 99 percent confidence interval is unacceptable. When an unacceptable value for the QCCS is obtained, recalibrate the instrument and reanalyze all samples up to the last acceptable QCCS.

At specified intervals determined by the QA program, the control charts should be updated. Cumulative means and new warning and control limits should be calculated. Bias for a given analysis is indicated by at least seven successive points on one side of the cumulative mean. If bias is indicated, analysis should be stopped until an explanation is found. The same QCCS should be used to establish all values on a given control chart to ensure continuity. Data from the QCCS standards should be logged on the appropriate QC forms.

3.2.6 Matrix Spikes

Matrix spikes are prepared for each extract or exchange procedure as listed in Table 3-1 and as described in the individual methods sections.

The sample selected for spiking should be of mid-range concentration. The spike recovery should be within 90 to 110 percent (95 to 105 percent for sulfate isotherms) of the known value of the spike. If this criterion is not met, two additional, different samples from the batch should be spiked and analyzed, and logged on the same QC form. If the spike recovery of either of the two additional samples fails to meet the 90 to 110 percent criterion (95 to 105 percent for sulfate isotherms), the laboratory or QA manager should be notified before the data for this parameter are reported.

For soil extract or exchange solutions, a matrix spike is prepared by spiking an aliquot of an extract solution with a known quantity of analyte prior to analysis. The calculated concentration of the added spike should be approximately equal to the endogenous level of the aliquot or 10 times the detection limit, whichever is larger, and should not exceed the linear range of the instrument. Also, the volume of the spike should be negligible in calculating the spike recovery. The spiked sample is analyzed side by side in the batch with the sample that was aliquoted.

3.2.7 Ion Chromatography Resolution

Perform an ion chromatography (IC) resolution test once per analytical run by analyzing a standard that contains sulfate, nitrate, and phosphate in concentrations that approximate those found in the IC analysis. If the resolution does not exceed 60 percent, the column should be replaced, and the resolution test should be repeated.

3.2.8 Quality Control Audit Sample

One QC audit sample (QCAS) of known concentration is run in each batch. Data from the QCAS should fall within the defined accuracy windows for the specific audit materials.

3.3 Data Entry and Record Keeping

3.3.1 Raw Data

All instrument print-outs, strip-charts, etc., should be identified with the following information: date and analyst's name, laboratory method and specific parameter measured, and batch and sample number. These raw data should be retained by the laboratory for ready retrieval as directed by the QA manager.

All observations made in the laboratory (i.e., weighings, extract volumes, and titrations) should be recorded in an appropriate log book or data sheet along with the above information required for instrument print-outs as well as all information required for calculations, e.g. (aliquot and final volumes) and all appropriate QC data as discussed in the preceding section. These log books or data sheets should be retained by the laboratory for ready retrieval as directed by the QA manager.

3.3.2 Reported Data

All required data should be reported to the recommended number of decimal places as indicated on the reporting forms. Copies of the data forms are provided in Appendix B.

Any data obtained using deviations from the established procedures should be tagged with the appropriate data qualifier (Table 3-4 lists data qualifiers developed for the DDRP). A detailed explanation of the deviation used to acquire the tagged data should accompany that data.

Table 3-4. Analytical Laboratory Data Qualifiers (Tags)

Data Qualifier (Tag)	Explanation
A	Instrument unstable.
B	Redone, first reading not acceptable.
F	Result outside criteria with consent of QA manager.
G	Result obtained from method of standard additions.
J	Result not available; insufficient sample volume shipped to laboratory.

(continued)

Table 3-4. (Continued)

Data Qualifier (Tag)	Explanation
L	Result not available because of interference.
M	Result not available; sample lost or destroyed by laboratory.
N	Result outside QA criteria.
P	Result outside criteria, but insufficient volume for reanalysis.
R	Result from reanalysis.
S	Contamination suspected.
T	Container broken.
U	Result not required by procedure; unnecessary.
X	No sample.
Y	Available for miscellaneous comments.
Z	Result from approved alternative method.

3.4 References

Blume, L. J., M. L. Papp, K. A. Cappo, J. K. Bartz, D. S. Coffey, and K. Thorton. 1987a. *Sampling Protocols for the Southern Blue Ridge Province Soil Survey.* Appendix A In: Coffey, D. S., J. J. Lee, J. K. Bartz, R. D. Van Remortel, M. L. Papp, and G. R. Holdren. *Direct/Delayed Response Project: Field Operations and Quality Assurance Report for Soil Sampling and Preparation in the Southern Blue Ridge Province of the United States Volume I: Sampling.* EPA/600/4-87/041a. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C.

Blume, L. J., D. S. Coffey, and K. Thornton. 1987b. *Field Sampling Manual for the National Acid Deposition Soil Survey.* Appendix A In: Coffey, D. S., M. L. Papp, J. K. Bartz, R. D. Van Remortel, J. J. Lee, D. A. Lammers, M. G. Johnson, and G. R. Holdren. *Direct/Delayed Response Project: Field Operations and Quality Assurance Report for Soil Sampling and Preparation in the Northeastern United States. Volume I: Sampling.* EPA/600/4-87/030. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C.

4.0 Sample Processing and Rock Fragment Determination

4.1 Overview

Sample processing includes sample drying, disaggregation, sieving, homogenization, and subsampling. Each of these is performed as sample processing steps in the preparation laboratory; homogenization and subsampling are also completed at the analytical laboratory. The objective of these procedures is to produce homogeneous subsamples for subsequent analyses of physical and chemical parameters. Also included in this section is the procedure used for determination of percent rock fragments.

The procedures presented here are specific to bulk sample preparation methods employed in the DDRP. Alternatives to these procedures are available in the published literature; for example, *Procedures for Collecting Soil Samples and Methods of Analysis for Soil Surveys* (USDA/SCS, 1972). Alternatives include, but are not restricted to, use of different sized sieves, determination of soil moisture on a subsample of sieved, but not air-dry, sample, different size classifications of rock fragments, and grinding of soil material to pass a No. 60 or No. 100 sieve.

4.1.1 Summary of Method

Sample tables constructed of polyvinyl chloride (PVC) and heavy nylon mesh are used to air dry the samples. Use of the mesh enhances air circulation and increases the rate of sample drying.

After a bulk soil sample has been determined to be air dry, it is ready to be disaggregated and sieved to remove rock fragments and to prepare the sample for homogenization and subsampling. The disaggregation and sieving areas should be covered with protective layers of kraft paper and cleaned after each sample has been sieved. Dust masks and protective clothing should be worn at all times. Ventilation and heating should be provided in the sieving area.

To obtain representative volumes of soil suitable for detailed analysis at the analytical laboratories, it is necessary to prepare homogenous subsamples from the less than 2-mm soil fraction through the use of a riffle splitter. The preparation laboratory prepares two different subsamples for: (1) analyses of physical and chemical parameters and, (2) elemental analysis of total carbon, nitrogen, and sulfur. The general analytical sample should weigh approximately 500 g, while the elemental analytical sample should weigh approximately 50 g. Each analytical sample is derived through homogenization and subsampling by the procedure described in Section 4.6.3.

During shipping to the analytical laboratory, the sample material within each container segregates by particle size and density. Therefore, each sample must be homogenized by thorough mixing prior to removal of aliquots for analysis. Mixing should be performed by riffle-splitting.

4.1.2 Interferences

The known interferences specific to the parameter being measured are detailed in the sections containing analysis procedures for that parameter. In sample preparation, all interferences are collectively termed contamination. Chemicals used in analyses are to be kept away from the drying area. Food, drinks, and smoking are prohibited in the drying area. A separate pair of gloves should be worn when handling each sample. The drying area should be damp-mopped at least once a week to control dust.

A source of compressed air is necessary to clean the surfaces of the equipment (e.g., rolling pins, sieves, and gloves) after processing each sample. However, because water and oil tend to accumulate in the tank and conduit, the air must be passed through a filter trap to collect vapor and liquid.

In addition to cleaning with compressed air, the surfaces of the processing equipment may be wiped with clean Kimwipes if soil is adhering to the rolling pin or to the frame of the sieve. Used tissues are discarded after each sample is processed to avoid contamination.

The riffle splitter is cleaned with compressed air after each sample is split. If the operator suspects that the riffle splitter is still not thoroughly clean, the riffle splitter should be washed with deionized water and allowed to air dry completely. The work area is cleaned with a brush or hand vacuum after each sample is processed. The work area should be vented with an operating fume hood.

4.1.3 Safety

The calibration standards, sample types, and most reagents pose little hazard to the analyst. However, protective clothing (laboratory coat and gloves), safety glasses, and dust masks should be worn.

4.2 Sample Collection, Preservation, and Storage

The procedures contained here are applicable to bulk soil samples (routine and duplicate) and to field audit samples. Bulk samples are those soil samples taken from a designated portion of a specific horizon. A bulk sample contains approximately one gallon of soil and generally weighs about 5.5 kg. The bulk samples are deposited in large plastic bags and placed within protective outer canvas bags. Field audit samples are quality evaluation (QE) samples; these samples are sieved, packaged, and shipped in the same manner as their associated routine samples. All samples should be stored at 4 °C.

4.3 Equipment and Supplies

4.3.1 Equipment Specifications

1. Riffle splitter, Jones-type; closed-bin, two-pan, 1.25-cm baffles (preparation laboratory).

2. Enclosed Drawer Riffle Sampler (American Society for Testing Materials [ASTM] D271) with four drawers, Fisher Scientific No. 04-940 and 04-940-5, or equivalent. Larger-sized splitters should not be used for this operation (analytical laboratory).

4.3.2 Apparatus

1. Fume hood.
2. Drying tables, PVC/nylon mesh.
3. Rolling pin, wooden.
4. Rubber stoppers.
5. Brass sieves, square-holed: 2-mm and 4.75-mm.
6. Clean sieving table and work area.
7. Air compressor, with in-line filter.
8. Balance, capable of weighing to 0.1 g.
9. Wide-mouth funnel.
10. Distribution pan.
11. Brush or hand vacuum.
12. Balance calibration weights, 3-5 weights covering expected range.

4.3.3 Reagents and Consumable Materials

1. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).
2. Kraft paper, 36" wide rolls.
3. Plastic gloves (unpowdered).
4. Small cellophane bags with twist ties.
5. Kimwipes.
6. Dust masks.
7. Nalgene bottles: 2-L, 500-mL, 125-mL.
8. Plastic bottles, 500-mL, wide mouth.
9. Bulk sample processing raw data forms (Appendix B, Figure B-3).
10. DDRP Label A rolls (Figure 3-1).

4.4 Calibration and Standardization

Calibration of the balance is detailed in Appendix A, General Laboratory Procedures.

4.5 Quality Control

The only quality control check applicable to this procedure is daily and weekly checks of the balance accuracy using three to five balance calibration weights covering the range of sample measurements.

4.6 Procedure

4.6.1 Sample Drying

1. Label a bulk sample processing raw data form (see Appendix B, Figure B-3) for each sample to be air dried.

2. Place two fresh sheets of kraft paper, approximately 1 m x 1 m in area, on the mesh partition of the drying table. With gloved hands, slowly spread the sample on top of the sheets of paper, taking care not to lose any soil off the paper or contaminate any adjacent samples.

   NOTE: In some cases, samples may be received from the field in more than one sample container (bag). Combine the contents of all containers comprising a single sample.

3. Disaggregate any large pedons that impede the spreading of the sample over the entire area of the paper. Place an additional sheet of kraft paper loosely over the sample.

4. Identify the sample by attaching the sample's processing raw data form to a hook attached to the drying table or other mechanism. The original canvas and plastic sampling bags should be kept on the floor beneath the sample as a second check on sample identity.

   NOTE: Immediately after a sample is spread to dry, field-moist pH is determined (Section 6.0).

5. Daily, stir the soil sample with gloved hands to facilitate drying.

6. For the first few days that a wet sample is spread, the bottom sheet of paper may need to be changed daily in order to alleviate excessive moisture accumulation. Any observations of fungal or algal growth should be noted on the bulk sample processing raw data form.

   NOTE: Soils high in clay may harden nearly irreversibly if allowed to dry without a preliminary disaggregation of medium and coarse pedons. An effort should be made during the air-drying procedure to disaggregate these pedons by physical manipulation with gloved hands while still somewhat moist or friable, before reaching an air-dry state.

7. Allow the sample to air dry until it is believed to be at or below the specified moisture content. This process generally takes about two days, although drying time may vary from one day to a week or more.

8. Subsample an aliquot for the air-dry moisture determination (Section 8.0).

4.6.2 Disaggregation and Sieving

A bulk sample must be weighed in its entirety before it is disaggregated and sieved in order to properly calculate the percentage of rock fragments in the sample.

1. Weigh the bulk sample while still in its plastic bag to the nearest 0.1 g and record this weight under "TOTAL BULK_WT" on the bulk sample processing raw data form. Large pieces of stems, moss, twigs, or roots are to be removed from a mineral sample before its bulk weight is determined.

2. Place a 1-m by 1-m sheet of kraft paper on top of the sieving table.

3. Place a 60-cm by 60-cm sheet of kraft paper on top of the table and spread small portions of the bulk sample within the confines of the sheet. Carefully examine the nature of the rock fragments within the sample and determine the amount of pressure to apply to the sample to disaggregate the soil pedons without fracturing or crushing the fragments.

4. Place another 60-cm by 60-cm layer of kraft paper over the sample and gently roll a wooden rolling pin across the sample; enough force should be applied to break up the pedons, but not so much that weathered rock fragments are crushed.

5. Place a portion of sample in the 2-mm mesh sieve and *gently* push the soil through the sieve with a rubber stopper. Attempt to include any soil adhering to rock fragments. Remove and discard any small roots remaining on the sieve.

6. Continue sieving until all of the less than 2-mm soil has passed through the 2-mm sieve.

7. Save the less than 2-mm sample in a 2-L Nalgene bottle pre-labeled with a DDRP Label A and place the bottle in cold storage until ready to proceed with homogenization and subsampling (sections 4.63 and 4.6.4). Continue processing the remaining rock fragments as described in Section 4.6.5.

4.6.3 Homogenization and Subsampling (Preparation Laboratory)

1. For each sample, pre-label one 500-mL and one 125-mL Nalgene bottle with the DDRP Label A information.

2. Position the two receiving pans under the riffle splitter.

3. Pour all of the less than 2-mm soil from the 2-L Nalgene sample bottle evenly across the baffles of the riffle splitter.

4. Transfer the soil from each receiving pan into the distribution pan and replace the receiving pans under the riffle splitter.

5. Repeat Step 4 *five* times in succession with the material in each receiving pan.
6. Pour the sample evenly across the baffles and place the soil from one receiving pan into the 2-L bottle.
7. Transfer the soil in the other receiving pan to the distribution pan and continue splitting as necessary until approximately 500 g of soil occupies one of the receiving pans.
8. Place the *entire* contents of the pan into the pre-labeled 500-mL bottle (general analytical sample).
9. Repeat the splitting using the remaining soil until approximately 50 g of soil occupies one of the receiving pans; transfer the *entire* contents of the pan into the pre-labeled 125-mL bottle (elemental analytical sample).
10. Transfer all leftover soil into the 2-L bottle to serve as an archive sample. The analytical samples are grouped by set ID and placed in cold storage until they are batched and shipped via overnight express service to the analytical laboratories. The archive samples are grouped by batch ID and remain in cold storage indefinitely.

4.6.4 Homogenization and Subsampling (Analytical Laboratory)

1. Pour the sample from the shipping bottle slowly and evenly across the slots of the splitter, keeping the drop height less than 2 inches to avoid excessive loss of dust. Repeat this procedure for 5 passes through the riffle splitter.
2. Place the split sample from one pan in the shipping bottle; label this as a laboratory reference sample and refrigerate at 4 °C.
3. Place the split sample from the other pan in a clean Nalgene bottle, label, and use for laboratory analysis.

NOTE: To mix the soil before removing an aliquot, the bottle should never be more than three-fourths full.

NOTE: Thoroughly clean the splitter and pans to prevent sample carry-over from one sample to the next.

After the sample has been homogenized, minimal bottle movement (transport, shaking, etc.) is warranted to eliminate possible sample resegregation by particle size and density. Bottles must remain closed (capped) at all times except during aliquot removal for each analysis. Bottles may remain at room temperature while analyses are being performed. Removal of an aliquot for a given analysis should be done by a random insertion of a clean sampler (spatula, scoop, etc.) into the bottle.

NOTE: If the bottle will not be used for aliquot extraction for more than 7 days, storage of the sample at 4 °C is required. Re-warm the sample to room temperature with the bottle closed (capped) prior to further analysis.

After all analyses have been completed and the results have been checked, the analytical samples are stored at 4 °C in the event that reanalysis is necessary.

4.6.5 Rock Fragment Determination

1. Save the rock fragments which could not pass through the 2-mm sieve (Section 4.6.2) and place them on the 4.75-mm sieve.

2. Retain in separate cellophane bags the material which passes through the 4.75-mm sieve and that which does not pass.

   NOTE: If field procedures do not include passing the sample through a 20-mm sieve, pass the material which was retained on the 4.75-mm sieve through a 20-mm sieve. Retain in a cellophane bag the material which passes the 20-mm sieve. Also retain and weigh the material which did not pass the 20-mm sieve; subtract this value from the orginal total bulk weight. Use the adjusted total bulk weight in Section 4.7.

3. Weigh to the nearest 0.1 g the fragments which passed through the 4.75-mm sieve but were retained by the 2-mm sieve. Record this weight on the bulk sample processing raw data form under "2- TO 4.75-MM ROCK FRAGMENTS". Then weigh the fragments that were retained by the 4.75-mm sieve. Record this weight under "4.75- TO 20-MM ROCK FRAGMENTS".

Place the rock fragment bags for each sample in the leftover plastic bag from the bulk sample. Make sure that a DDRP Label A with the appropriate sample code and set ID is affixed to the bag. Save all rock fragment bags, organized by set ID, until instructed by the soil sampling task leader to discard or transfer the fragments to another location. It is *not* necessary to keep the rock fragments in cold storage.

4.7 Percent Rock Fragment Calculations

The following calculations may be performed by computer calculation after the raw data are entered. If so, it is still advantageous to manually check a few samples using these calculations to understand the procedure and to test the accuracy of the computer program. The percentages of fine gravel (RF_FG) and medium gravel (RF_MG) are calculated as follows:

$$\text{RF\_FG} = \frac{\text{2- to 4.75-mm rock fragments}}{\text{Total Bulk wt.}} \times 100$$

$$\text{RF\_MG} = \frac{\text{4.75- to 20-mm rock fragments}}{\text{Total Bulk wt.}} \times 100$$

4.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water,* D-1193-77 (reapproved 1987). ASTM, Philadelphia, Pennsylvania.

U.S. Department of Agriculture/Soil Conservation Service. 1972. *Procedures for Collecting Soil Samples and Methods of Analysis for Soil Surveys.* Soil Survey Investigations Report No. 1, United States Department of Agriculture, U.S. Government Printing Office, Washington, D.C.

5.0 Bulk Density Determination

5.1 Overview

Density is defined as weight per unit volume and is expressed in units of g/cm^3. The bulk density of a soil is defined as the weight of dry soil per unit volume including the pore space. For mineral soils, bulk density generally ranges from 0.6 to 2.0 g/cm^3. With increasing organic matter content, soils generally exhibit a decrease in bulk density because organic matter has higher porosity and lower density than mineral particles of the same diameter.

5.1.1 Summary of Method

In the DDRP surveys, the clod method is the primary method for determining bulk density. Where possible, three replicate clod samples are extracted from each horizon. The average bulk density of the replicates is assumed to be the bulk density of that particular horizon. Analysis of the clods is based on the method described in the USDA/SCS (1984), Kern and Lee (1989), and Kern et al. (in preparation).

Two alternate methods are also presented for soil horizons that fail to yield satisfactory clods. One method is volume replacement (VR), a method similar to one described by Flint and Childs (1984), which utilizes a known volume of small foam beads packed into a cylinder to replace a selected volume of soil excavated from a given horizon. Subtracting the initial from the final volume yields the estimated volume of sample collected. The other method is a volume filling (VF) method that is used if the clod or VR methods do not produce representative samples. The volume of this type of sample is based on the absolute height of a 250-mL beaker, which is a constant 300 cm^3. The known volume samples are processed in a manner similar to the method described in Blake (1965).

5.1.2 Interferences

Evaporating dishes used in the clod method must be thoroughly cleaned after each use, as their weights are pre-determined and used in the calculation of results. Tongs or finger cots should be used when transferring the dishes from one location to another.

5.1.3 Safety

5.1.3.1 Clod Method--

Laboratory personnel should use caution when working around the muffle furnace because temperatures of up to 450 °C are common. The furnace should be activated only in an operable fume hood. Heat resistant gloves may be needed when placing samples in the furnace. The furnace must be adequately vented and protected from human contact and combustible materials.

Extra precaution must be taken in the use of the Saran powder and acetone solution (see Section 5.3.2, Step 2). When mixed, the resulting solution has a tendency to volatilize hydrogen chloride gas which can cause deleterious health effects. The solution should be used only in an operating vented fume hood. Half mask and cartridge-type respiratory protection, gloves, and laboratory coat should be worn.

In the field, exposure to Saran solution through inhalation and skin contact must be minimized. Gloves and respiratory protection are recommended. Use solution only in a well-ventilated area downwind of the sampling site.

5.1.3.2 Volume Methods--

The safety concerns cited above do not apply to the VR or VF methods. Protective clothing (laboratory coat and gloves), safety glasses, and dust masks should be worn.

5.2 Sample Collection, Preservation, and Storage

Clod samples are fist-sized, structurally intact, bulk density samples taken from designated horizons. In the field, each clod is wrapped in a hairnet and dipped briefly in a 1:5 Saran:acetone solution to help maintain the clod structure and reduce moisture loss from the clod during transport and storage. Each clod is labeled, covered by a small plastic bag, and placed in a special box with dividers.

Known volume bulk density samples are taken from horizons where clods are unobtainable. There are two types of known volume samples used in the DDRP: volume replacement and volume filling samples. These bulk density samples are packaged in small, pre-labeled plastic bags in much the same manner as the bulk soil samples.

Samples are stored at 4 °C until analysis.

5.3 Equipment and Supplies

5.3.1 Apparatus

The following items are used in both the clod and volume methods:

1. Convection oven.

2. Desiccator and desiccant.

3. Brass sieve, squared-holed, 2 mm.

4. Forceps.

The following additional apparatus is needed for the clod method:

1. Fume hood.

2. Balance, capable of weighing to 0.1 g.

3. Organic vapor mask, cartridge-type.
4. Beakers, 1000-mL and 2000-mL.

5. Ring stand.

6. Test tube clip, adjustable.

7. Evaporating dishes, pre-numbered, tolerance to 450 °C.

8. Furnace gloves.

9. Tongs.

10. Muffle furnace.

11. One-gallon metal cans with airtight lids (paint cans).

12. Magnetic stirrer and stir bars, or long stir sticks.

13. Shower curtain rod.

14. Stop watch.

15. Thermometer, National Bureau of Standards (NBS)-traceable

16. Balance calibration weights, 3-5 weights covering expected range.

17. Class "P" balance weight, 500 g.

The only item needed for the volume methods in addition to the four listed previously is:

1. Balance, capable of weighing to 0.01 g.

5.3.2 Reagents

NOTE: All reagents listed are for the clod method. The volume methods do not require any reagents.

1. Acetone, industrial grade.

2. Saran:acetone clod dipping mixture, approximately 1:5 by weight.

   NOTE: The clod dipping solution must be mixed only under an operating vented fume hood. The operator must wear a cartridge-type organic vapor mask and laboratory coat while mixing the dipping solution.

   For the DDRP, the Saran powder is prepackaged in 540-g allotments. One packet mixed with approximately 3400 mL of acetone provides a nearly 1:5 by weight mixture resembling light syrup. One-gallon paint containers are used for mixing and storing the solution. Slowly add the contents of each packet to the acetone while stirring. Continue stirring to ensure thorough dissolution of the powder. The solution normally is well mixed when it has the color and consistency of amber syrup and there is no gummy Saran residue on the edges or bottom of the container. If the solution is a milky color, additional mixing is required. The powder has a tendency to precipitate and clump around a container's lower rim when mixed with acetone. To prevent this, use a long stir stick and thoroughly scrape the inner rims. If possible, use a magnetic stirrer and a stir bar to mix the ingredients in a beaker until well blended, then transfer mixture to paint container for storage.

   After mixing the solution, the container should be capped as tightly as possible to prevent leakage of the solution or evaporation of the acetone.

3. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

5.3.3 Consumable Materials

Consumable items required for the clod method are:

1. Paper bags, pre-labeled.

2. Plastic bags, large.

Consumable items required for the known volume methods are:

1. Paper bags, pre-labeled.

2. Clod bulk density raw data form (Appendix B, Figure B-4).

3. Known volume bulk density raw data forms (Appendix B, Figure B-5).

4. Known volume log book (known volume method).

5. Volume data from sample receipt log book (known volume method).

5.4 Calibration and Standardization

Calibration of the balance is detailed in Appendix A, General Laboratory Procedures.

5.5 Quality Control

NOTE: This applies only to the clod method.

Record the dry weight and submerged weight of a 500-g Class "P" balance weight immediately before and after a run of samples. These weights are used to verify proper balance operation and are charted on a daily basis.

5.6 Procedure

5.6.1 Clod Method

NOTE: All raw data obtained from the clod analysis are recorded on the clod bulk density raw data form (see Appendix B, Figure B-4). For each clod to be analyzed, record the set ID, sample code, and the replicate number on the form. Examine the label attached to the clod and record the number of field dips performed by the sampling crew under "FIELD_DP" on the form. Weigh the clod, without removing the label, to the nearest 0.1 g and record this weight under "FIELD_WT/MOIST".

1. Suspend the clod in a convection oven and dry overnight at 105 °C for mineral samples, or 60 °C for organic samples. The following morning, transfer the clod into a desiccator for 30 minutes. Weigh the sample to the nearest 0.1 g and record this weight under "FIELD_WT/DRY".

2. Hang the clod on a suspended curtain rod within an operating vented fume hood. Dip the clod into a container of 1:5 by weight Saran:acetone mixture (see Section 5.3.2, Step 2) for three seconds and then allow the coating to dry for approximately 15 minutes. Do not allow the mixture to impregnate that portion of the hairnet hanging above the top of a clod.

NOTE: Alternately, the clod may be sprayed with water just prior to dipping in the Saran:acetone solution. The water reduces the penetration of Saran into the clod and produces a frost appearance, indicating the solution has coated the outside of the clod. Whichever alternative is chosen, it is important that the same technique be used on all samples.

3. Apply additional dips as necessary until the clod does not produce excessive bubbles and a coating of Saran is obtained that appears to be impervious to water. Usually three to six dips is sufficient for most clods. Record the total number of dips made in the laboratory under "LAB_DP", then reweigh the clod to the nearest 0.1 g and record this weight under "LAB_WT". Also perform and record the dry-weight quality control check (Section 5.5).

4. Add approximately 1600 mL of deionized water to a 2000-mL beaker. Place the beaker of water on a balance and tare. Record the temperature of the water under "TEMP" so that the density of the water can be calculated. Also perform and record the submerged weight quality control check (Section 5.5).

5. Suspend the clod over the beaker by attaching the top of the hairnet to the test tube clip, then lower the clod gently into the water until the top of the clod is entirely submerged. Promptly, after three seconds, record the weight displayed on the balance to the nearest 0.1 g under "CLOD_H2O". If the clod floats, forcibly submerge it by pushing down with forceps and record the weight. Note on the raw data form, with a "Y" under "FLOAT", that the clod floated. Retare the balance before proceeding with other clods.

   NOTE: When submerging, ensure that the clod is not touching the edge of the beaker and that the clod label hangs freely. Occasionally, air bubbles may rise from the clod and the weight reading on the balance does not stabilize but steadily decreases. This occasionally occurs in clods sampled from relatively porous surface horizons and simply indicates that all of the primary macropores along the exterior of the clod were not thoroughly water-sealed. By reading the weight immediately after submersion, error from this source of instability is minimized. Note the bubbling on the raw data form under "COMMENTS". Also note any other problem, such as a broken clod, under "COMMENTS".

6. After submersion, place the clod in a pre-numbered evaporating dish and record the dish number on the raw data form under "CRUC_NO". Remove as much of the clod label and hairnet as possible and place in a large plastic bag with others from the same run.

7. Place the evaporating dish plus clod in a muffle furnace equilibrated at 400 °C. The muffle furnace must be within an operating vented fume hood. Allow the Saran coating to be burned off the clod surface for two hours. Allow the furnace to cool, then carefully remove the evaporating dish from the muffle furnace. After the clod has cooled thoroughly, place it in a pre-labeled, paper bag.

8. Disaggregate the clod through a 2-mm sieve. Weigh any rock fragments retained on the sieve to the nearest 0.01 g and record this weight under "R_FRAG". Place the rock fragments into the paper bag and archive all such bags.

Alternatively, the clods may be soaked in water and dispersing agent to aid in disaggregation. Wet sieving may be most efficient, followed by drying of coarse fragments at 105° C.

5.6.2 Known Volume Method

NOTE: Known volume bulk density samples are shipped from the field in small, plastic bags. Upon passing the sample receipt verification, these samples can be placed out to air dry in the drying area (see Section 4.6.1). The drying facilitates the transfer of the entire sample from its plastic bag into a pre-labeled paper bag. Do not remove *any* material from the bag, even if the material is thought to be morphologically different from the type of horizon sampled.

NOTE: Record the set ID and sample code of the VR or VF sample on the known volume bulk density raw data form (see Appendix B, Figure B-5).

1. Weigh the paper bag plus sample to the nearest 0.01 g and record this weight under "AIR_WT".

2. Place the bag in a convection oven equilibrated at 105 °C for mineral soils and 60 °C for organic soils. Allow the sample to oven dry overnight.

3. The following morning, remove the sample from the oven and allow to cool for 30 minutes. Weigh the sample to the nearest 0.01 g and record this weight under "OD_WT".

4. Sieve the contents of the bag through a 2-mm sieve to remove any rock fragments. Weigh the rock fragments to the nearest 0.01 g and record this weight under "R_FRAG". Place the rock fragments in the paper bag and archive all such bags.

5. Transcribe the computed volume (V_i minus V_f) for a VR sample from the sample receipt log book to the "VOL" column on the raw data form. For a VF sample, 300 cm^3 can be automatically entered under "VOL".

5.7 Calculations

5.7.1 Clod Method

It is assumed that the weight of each two-second Saran coating applied in the field is equal to the weight of each three-second coating applied in the laboratory, as some of the dipping solution normally is absorbed into the clod when it is applied in the field.

It is assumed that the specific gravity of air-dry Saran is 1.30 g/cm^3 and that the coating loses 15 percent of its weight upon oven-drying. It is assumed that the particle density of the rock fragments is 2.65 g/cm^3.

It is assumed that the average gross weight of the hairnet and clod label is 1.88 g and the net weight of the submerged portion of the hairnet is 0.20 g.

The following calculations may be performed by computer after the raw bulk density data are entered. If so, it is advantageous to manually check a few samples using these calculations to understand the procedure and to test the accuracy of the computer program. A list of temperature-corrected water density values is provided in Table 5-1.

Table 5-1. Density of Pure Water[a]

Temp °C	Water Density
13.0	0.9992
14.0	0.9991
15.0	0.9990
16.0	0.9988
17.0	0.9987
18.0	0.9986
19.0	0.9984
20.0	0.9982
21.0	0.9980
22.0	0.9978
23.0	0.9976
24.0	0.9973
25.0	0.9971
26.0	0.9968
27.0	0.9965
28.0	0.9963
29.0	0.9960
30.0	0.9957
31.0	0.9954
32.0	0.9951
33.0	0.9947
34.0	0.9944
35.0	0.9941

[a] Adapted from List (1984).

Use the following calculations to derive the weights and volume of the air-dry and oven-dry Saran coatings:

$$\text{SARAN\_WT (g)} = \frac{[(\text{FIELD\_DP} + \text{LAB\_DP}) \times (\text{LAB\_WT} - \text{FIELD\_WT/DRY})]}{\text{LAB\_DP}}$$

$$\text{OD SARAN\_WT (g)} = \text{SARAN\_WT} \times 0.85$$

$$\text{SARAN VOL (cm}^3\text{)} = \frac{\text{SARAN\_WT}}{1.30}$$

Use the following calculations to derive the volumes of rock fragments, water displacement, and soil/pore fraction:

$$\text{R\_FRAG VOL (cm}^3\text{)} = \frac{\text{R\_FRAG}}{2.47}$$

$$\text{WATER VOL (cm}^3\text{)} = \frac{\text{CLOD\_H2O}}{\text{DENSITY OF WATER}}$$

$$\text{SOIL/PORES VOL (cm}^3\text{)} = \text{WATER VOL} - (\text{R\_FRAG VOL} + \text{SARAN VOL})$$

Finally, use the following calculation to derive the oven-dry bulk density (BD_CLD) for the individual clod:

$$\text{BD\_CLD (g/cm}^3\text{)} = \frac{\text{LAB\_WT} - (\text{R\_FRAG} + \text{OD SARAN\_WT} + 1.88)}{\text{SOIL/PORES VOL} - 0.20}$$

5.7.2 Known Volume Method

The particle density for rock fragments in a VR bulk density sample is derived individually by a submersion technique similar to that used in the clod analysis. It is assumed that the particle density for rock fragments in a VF bulk density sample is 2.65, unless specific particle density measurments are made of different classes of rock fragment types.

The following calculations for known volume bulk density (BD_KV) may be performed by computer. It is advantageous to manually check a few samples using these calculations to understand the procedure and to test the computer program.

$$\text{FINES\_WT (g)} = \text{OD\_WT} - \text{R\_FRAG}$$

$$\text{BD\_KV (g/cm}^3\text{)} = \frac{\text{FINES\_WT}}{\text{VOL} - (\text{R\_FRAG} \div \text{particle density})}$$

5.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water,* D-1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Blake, G. R. 1965. In Black, C. A. (ed.) *Methods of Soil Analysis, Part 1.* American Society of Agronomy, Madison, Wisconsin.

Flint, A. L., and S. Childs. 1984. Development and Calibration of an Irregular Hole Bulk Density Sampler. *Soil Science Society of America Journal* 48 (2):374-378. Soil Science Society of America, Madison, Wisconsin.

Kern, J. S., and J. J. Lee. 1989. Evaluation of Two Alternative Bulk-Density Methods. *Agronomy Abstracts.* American Society of Agronomy, Madison, Wisconsin.

Kern, J. S., M. L. Papp, J. J. Lee and L. J. Blume. In preparation. Appendix A In Kern, J. S. and J. J. Lee, *Direct/Delayed Response Project: Field Operations and the Mid-Appalachian Region of the United States,* U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C.

USDA/SCS. 1984. *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples. Soil Survey Investigations Report No. 1.* U.S. Government Printing Office, Washington, D.C.

6.0 Field-Moist pH Determination

6.1 Overview

The pH is defined as the negative logarithm of the activity of hydrogen ions (H^+). The H^+ activity is a measure of the "effective" concentration of hydrogen ions in solution; it is always equal to or less than the true concentration of hydrogen ions in solution. Values range from pH 1 to pH 14, with pH 1 most acidic, pH 7 neutral (at 25 °C), and pH 14 most alkaline. Each pH unit represents a tenfold change in H^+ activity (i.e., a pH 4 solution is 10 times as acidic as a pH 5 solution).

When the pH of a sample solution is measured, the hydrogen ions come into equilibrium with the ion exchange surface (glass) of a calibrated pH electrode, which creates an electrical potential. This voltage difference is measured by the pH meter in millivolts (mv), which is then converted and displayed as pH units.

6.1.1 Scope and Application

This method is applicable to the determination of pH in soil samples. For the Direct/Delayed Response Project (DDRP), field-moist pH is determined in the preparation laboratory using an Orion Model 611 pH meter and an Orion Ross combination pH electrode. The method has been written assuming that the Orion meter and electrode are used (Orion, 1983). The method, however, can be modified for use with other instrumentation meeting specifications equivalent to those given in Section 6.3.1.

The applicable pH range for soil solutions is 3.0 to 11.0.

6.1.2 Summary of Method

Immediately after a sample is spread to air dry, a field-moist subsample is collected and pH in deionized water (DI) is determined. The pH can vary as much as one pH unit between the supernatant and soil sediment. Always place the electrode junction at the same distance (approximately 3 mm) above the surface of the soil sediment to maintain uniformity in pH readings.

6.1.3 Interferences

Factors that normally affect the measurement of pH are: (1) electrolyte content of the extractant; (2) soil-to-solution ratio; (3) temperature and CO_2 content of the extractant; (4) errors that occur with instrument calibration, standard preparation, and liquid junction potential; (5) organic and inorganic constituents; (6) length of time the soil and solution stand before they are measured; and (7) technique used in reading the sample suspension.

Soils high in salts, especially sodium, may interfere with the pH reading and the electrode response time. Clay particles may clog the liquid junction of the pH reference electrode junction, slowing the electrode response time; thoroughly rinse the electrode with DI water between sample readings to avoid this problem. Wiping the electrode dry with cloth, laboratory tissue, or similar materials or removing the electrode from solution when the meter is not on standby may cause electrode polarization.

The initial pH of a nonalkaline soil will usually be as much as 0.5 pH unit greater than the pH taken after the sample has set for 30 minutes or longer. The pH can vary as much as 1.0 pH unit between the supernatant and soil sediment. Always place the electrode junction at the same distance (approximately 3 mm) above the surface of the soil sediment to maintain uniformity in pH readings.

6.1.4 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids should be restricted to a fume hood.

6.2 Sample Collection, Preservation, and Storage

The subsample used for determination of field-moist pH is taken from the bulk soil sample immediately after it has been spread to air dry (see Section 4.6.1). The subsample is mixed with DI water conforming to standards for ASTM Type I reagent grade water (ASTM, 1984). The sample is stored at 4 °C prior to analysis.

6.3 Equipment and Supplies

6.3.1 Equipment Specifications

1. Digital pH/mV meter, capable of measuring pH to ±0.01 pH unit, potential to ±1 mV, and temperature to ±0.5 °C. The meter must also have automatic temperature compensation capability (Orion Model 611 or equivalent).

2. A combination pH electrode, made of high quality, low-sodium glass. At least two electrodes (one as a backup) should be available. An Orion Ross combination pH electrode or equivalent with a retractable sleeve is recommended. Do not use a Gel-type reference electrode.

3. Balance, capable of weighing to 0.1 g

4. Balance calibration weights, 3-5 weights covering expected range.

6.3.2 Apparatus, Consumable Materials, and Reagents

1. National Bureau of Standards (NBS)-traceable thermometer.

2. Glass stirring rods.

3. 125-mL Nalgene bottles.

4. 25-mL and 50-mL plastic containers.

5. pH calibration buffers (pH 4.0 and 7.0)--Commercially available pH calibration buffers (NBS-traceable) at pH values of 4.0 and 7.0 (two sets from different sources for calibration and quality control checks).

6. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

7. Potassium chloride (3 M)--Dissolve 224 g KCl in DI water and dilute to 1 L.

8. Sodium hydroxide (NaOH) pellets.

9. Weighing pans, disposable.

10. Field-moist pH raw data form (Appendix B, Figure B-6).

11. Field-moist pH log book.

6.4 Calibration and Standardization

NOTE: For storage and readings, the electrode must be immersed to cover the liquid junction of the reference electrode (typically about 3 cm). Rinse the electrode with DI water between each sample and each buffer to prevent solution carryover. Do not rub or blot the electrode dry because this may produce a static electric charge and polarize the electrode.

6.4.1 Instrument Preparation

1. Plug in the instrument and verify that the control knob is on "STD BY." Allow at least 30 minutes for instrument warm-up prior to use.

   NOTE: If instrument is used frequently, leave on and in "STD BY" mode between uses.

2. Connect the combination electrode to the meter. Consult the pH electrode manual for the proper procedure.

3. Verify that the level of reference filling solution (3 M KCl) in the electrode is just below the fill hole and that the fill hole is uncovered during measurement (slide the plastic sleeve down).

4. Calibrate the meter for temperature weekly using a two-point standardization (one point at approximately 5 °C to 10 °C and the other point at room temperature).

   a. Room temperature--Place the electrode and an NBS-traceable thermometer into DI water which is at room temperature. Swirl the electrode for 5 to 10 seconds.

   b. Turn the knob on the meter to "TEMP." Using a small screwdriver adjust the display, using the "TEMP ADJ" screw on back of the pH meter, to the temperature reading of the thermometer.

   c. Cold temperature--Place the probe and the NBS-traceable thermometer into a 250-mL beaker containing cold DI water (5 to 10 °C). Repeat Step b by adjusting the display with the "TEMP SLOPE" screw on the back of the meter.

   d. Continue steps a through c until no further adjustments are necessary and record all values in the logbook.

6.4.2 Calibration with Buffers

1. Check the meter temperature calibration daily with a beaker of room temperature, DI water and an NBS-traceable thermometer. If the display differs from the NBS-traceable thermometer by more than 1.0 °C, complete adjustments as described in Section 6.4.1, above.

2. Pour fresh pH 7.00 and pH 4.00 buffer solutions into labeled 50-mL beakers (one "RINSE", one "CALIBRATION," and one "CHECK" beaker for each buffer). Rinse all beakers three times and fill with the appropriate buffer solutions.

3. Rinse the electrode with DI water. Place the electrode into the pH 7.00 "RINSE" beaker and swirl for 40 seconds. Place the electrode into the "CALIBRATION" beaker, turn the knob to "pH", swirl for 30 to 60 seconds (or until the pH reading is stable), and read the value on the display. Consult the pH-temperature chart, Table 6-1. Use the "CALIBRATE" knob to adjust the pH reading on the meter to the theoretical pH of the buffer solution at the appropriate temperature.

4. Repeat Step 3 for pH 4.00 buffer using the "% SLOPE" knob to adjust the pH reading.

5. Repeat steps 3 and 4 until both the pH 7.00 and the pH 4.00 buffers agree with the theoretical pH of the buffer solution at the appropriate temperature.

6. Check the standardization using the buffer solutions in the "CHECK" beakers. If the values differ by more than ±0.03 units from the theoretical value, repeat the standardization process. When the meter standardization is acceptable, record the pH and temperature readings for each buffer solution in the pH logbook.

Table 6-1. pH Values of Buffers at Various Temperatures

Temperature						
25 °C	0 °C	5 °C	10 °C	20 °C	30 °C	40 °C
1.68	1.67	1.67	1.67	1.67	1.68	1.69
3.78	3.86	3.84	3.82	3.79	3.77	3.75
4.01	4.00	4.00	4.00	4.00	4.02	4.03
6.86	6.98	6.95	6.92	6.87	6.85	6.84
7.00	7.11	7.08	7.06	7.01	6.98	6.97
7.41	7.53	7.50	7.47	7.43	7.40	7.38
9.18	9.46	9.40	9.33	9.23	9.14	9.07
10.01	10.32	10.25	10.18	10.06	9.97	9.89

6.4.3 Maintenance

1. Weekly, drain the 3 M KCl filling solution from the electrode using a disposable pipet with Teflon tubing attached.

2. Refill the electrode chamber with the 3 M KCl filling solution and rinse by inverting the electrode. Drain the solution as in Step 1.

3. Refill the electrode with the filling solution to just below the fill hole.

4. Gently spin the electrode overhead for approximately 1 minute by the leader to remove any air bubbles. Be careful to stand clear of any obstacles when swinging the electrode.

6.4.4 pH Meter Electronic Checkout

NOTE: This procedure should be performed whenever a new pH meter is set up or when calibration problems occur.

1. Connect the shorting strap as outlined in the Orion pH meter manual.

2. Turn the "TEMP ADJ" and "TEMP SLOPE" screws fully counterclockwise and record the display pH value (turn knob to "pH" position).

3. Turn the "TEMP SLOPE" screw 7.5 turns clockwise and record the display pH value. The difference between the "TEMP SLOPE" value in Step 2 and Step 3 should be between 7.0 and 15.0.

4. Turn the "TEMP ADJ" screw until a value between 50.0 ± 0.1 appears on display.

5. Press the test button. A value of 42.2 ± 2.0 should appear on the display when the knob is in the "TEMP" position. If this value is not displayed, keep depressing the test button and use the "TEMP SLOPE" screw to adjust the reading to 4.0 ± 1.0. Release the test button and use the "TEMP ADJ" screw to obtain a reading of 50.0 ± 0.1. Press the test button again. The reading should be 42.2 ± 2.0. Repeat this procedure several times if the value is not in range.

6.4.5 Electrode Etching Procedure

NOTE 1: Use *extreme caution* when using the NaOH pellets. Be sure to wear gloves, eye protection, and a rubber apron.

NOTE 2: If the electrode response is sluggish or if the instrument cannot be standardized, the following procedure is recommended for cleaning the ceramic junction of the electrode and improving the electrode response time.

NOTE 3: Etch electrodes in groups of three when possible. Prepare a fresh NaOH solution for each group of electrodes.

1. Drain the filling solution from the electrode.

2. Rinse the filling chamber with DI water and drain it.

3. Refill the chamber with DI water.
4. Prepare a 50 percent (w/v) NaOH solution by *slowly* adding 30 g of NaOH to 30 mL of DI water.
5. Gently stir the solution with up to three electrodes to dissolve the NaOH. The solution will be very hot and may boil and splatter; *caution must be used.*
6. Stir the solution an additional 2 minutes with the electrodes.
7. Rinse the electrodes with DI water.
8. Rinse the electrodes in pH 7.00 buffer for 2 minutes.
9. Drain the DI water from the filling chambers.
10. Refill each electrode with 3 M KCl, agitate the electrodes, and drain the chambers.
11. Refill the chambers once more with 3 M KCl and spin each electrode from the leader to remove air bubbles.

6.5 Quality Control

6.5.1 Initial Quality Control Check

1. Rinse and fill two beakers with pH 4.00 quality control (QC) solution. Use a different batch of traceable stock buffer solution than that used for calibration.
2. Rinse the electrode by swirling it in the rinse beaker for 15 to 30 seconds.
3. Insert the electrode into the measurement beaker.
4. Turn the knob to "pH". Wait until the reading seems fairly consistent, then note the time and pH values on a loose sheet of paper. If the pH reading does not vary by more than 0.02 pH units in one direction after a 1-minute interval, the reading is considered stable. Record the stable pH and temperature readings in the logbook.

6.5.2 Routine Quality Control Checks

NOTE: The pH 4.00 QC solution is analyzed at the beginning of a batch and at the end of a batch. The quality control check sample (QCCS) also is analyzed at intervals within the batch as specified by the quality assurance program.

1. Measure and record the QC solution by following the instructions in Section 6.5.1.
2. If the measured QC solution pH is acceptable (pH 4.00 ±0.05), proceed with routine sample pH determinations.
3. If the QC solution pH is not acceptable, follow the steps below until an acceptable value is obtained:

   a. Repour the pH 4.00 QC solution into a beaker and reanalyze.

   b. Clean the reference junction of the electrode.

   c. Check that the wiring straps into the meter are firmly connected and perform the electronic check as described in Section 6.4.4.

4. If the pH meter requires recalibration to obtain an acceptable QC reading, make a notation in the pH logbook. Determine which samples should be reanalyzed. Reanalyze all samples back to the last acceptable QC check.

6.5.3 *Quality Control/Quality Evaluation Samples*

Replicates--Ten percent of the samples in each batch should be analyzed in duplicate. The difference should be 0.15 pH units or less.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy window provided by the QA manager.

NOTE: Because the pH is measured immediately after a sample is spread to air dry, the number of samples in each run varies. It is necessary to adhere to all calibration protocols and QC specifications for all runs, regardless of size.

6.6 Procedure

6.6.1 *Sample Preparation*

1. After spreading and stirring the field-moist soil, scoop approximately 50 g of mineral soil or 15 g of organic soil into a 125-mL Nalgene bottle and record the sample code on the label of the bottle. Refrigerate the bottles at 4 °C until the analyst is ready to begin a run.

   NOTE: Some soils may be in a saturated state when received. Follow the procedure as stated; however, note the saturated condition of the soil on the bulk sample processing raw data form.

2. Place approximately 20 g of mineral soil or 5 g of organic soil into a pre-numbered 25-mL plastic container. Add 20 mL of DI water for mineral soils, or 25 mL for organic soils. Record the sample code and the container number on the field-moist pH raw data form.

3. Allow the sample to absorb the solution for approximately 60 seconds, then thoroughly stir the soil-solution mixture for 10 seconds with a glass stirring rod. Rinse the rod with DI water after stirring each sample. Stir again for 10 seconds after 15, 30, 45, and 60 minutes. Allow the suspension to settle for 30 minutes.

6.6.2 *Sample Measurement*

1. Place the pH electrode in the supernatant of the soil suspension. For mineral soils, the electrode junction is to be below the solution surface and above the soil-solution interface. Although organic soils normally absorb all of the free water available, an

acceptable reading generally is obtained if the electrode junction is below the meniscus of the organic material.

2. Record the pH of each sample (PH_MP) on the field-moist pH raw data form. Transcribe the pH values onto the appropriate entry field of each bulk sample processing raw data form (Appendix B, Figure B-3).
3. After the pH measurements are completed, store the electrode in storage solution. Do not allow the sensing element or reference junction to dry out. The level of the storage solution should be one inch below the filling solution level. The electrode sleeve is to be closed during storage. Check periodically to ensure that the electrode reservoir is full of storage solution.

6.6.3 Cleanup

1. Copiously rinse the electrode and glassware with DI water.
2. Cover the fill hole of the electrode with the plastic sleeve and store the electrode in 3 M KCl.
3. Make sure the meter is on "STD BY".

6.7 Calculations

No calculations are required to obtain pH values. Replicate measurements of the same sample or of duplicate samples should not be averaged.

6.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water,* D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Orion Research Incorporated. 1983. *Instruction Manual - Model 611 pH/millivolt meter.* Orion, Cambridge, Massachusetts.

7.0 Organic Matter Determination by Loss-On-Ignition

7.1 Overview

Loss-on-ignition (LOI) is the method used to determine an approximation of percent organic matter of soil samples. Because organic samples are oxidized at high temperatures, percent organic matter can be calculated on a weight-loss basis. From the percent organic matter, the percent organic carbon can be estimated. In the DDRP, LOI was used to classify samples as mineral or organic for subsequent analysis purposes. Organic material has between 12 and 18 percent organic carbon depending on the clay content of the mineral material (USDA/SCS, 1975). A 20 percent LOI was selected as the definition point, which corresponds to approximately 12 percent organic carbon.

7.1.1 Summary of Method

Oven-dried soil samples are ashed in a muffle furnace to remove organic material. The difference in pre- and post-ashing weights is used to calculate percent organic content. A modified version of the method described in MacDonald (1977) is used.

7.1.2 Interferences

Crucibles must be thoroughly cleaned after each use, as the crucible weights are predetermined and used in the calculation of results. Tongs or finger cots should be used when transferring crucibles from one location to another.

Caution should be used when interpreting the results of low organic content soil. In addition to organic matter, structural water and some soluble salts are commonly lost when heated to 450 °C.

7.1.3 Safety

Laboratory personnel should use caution when working around the muffle furnace, as temperatures of up to 450 °C are common. The furnace should be activated only in an operable fume hood. Heat resistant gloves may be needed when placing samples in the furnace. The furnace must be adequately vented and protected from human contact and combustible materials.

7.2 Sample Collection, Preservation, and Storage

A subsample is taken from the bulk soil sample after it has been spread to air dry (see Section 4.6.1). Samples may be stored at 4 °C until ready for analysis.

7.3 Equipment and Supplies

7.3.1 Apparatus

1. Balance, capable of weighing to 0.01 g.

2. Small crucibles, pre-numbered.

3. Tongs.
4. Desiccator, with desiccant and crucible plate.
5. Muffle furnace in operating fume hood.
6. Convection oven.
7. Balance calibration weights, 3-5 weights covering expected range.

7.3.2 Consumable Materials

1. Finger cots.
2. Furnace gloves.
3. Loss-on-ignition raw data forms (Appendix B, Figure B-7).
4. Loss-on-ignition log book.

7.4 Calibration and Standardization

Calibration of the balance is detailed in Appendix A, General Laboratory Procedures.

7.5 Quality Control

NOTE: Refer to Section 3.2 for additional information concerning these internal quality control (QC) checks.

Replicates--One sample from each batch should be analyzed in duplicate. The percent relative standard deviation (%RSD) should be 15 percent or less.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy window provided by the quality assurance (QA) manager.

7.6 Procedure

NOTE: The LOI analysis can be performed at any time while the samples are air drying. The data obtained are to be recorded on the loss-on-ignition raw data form (see Appendix B, Figure B-7).

1. Fill a small pre-numbered and pre-weighed crucible about two-thirds full of soil. Record the sample code and crucible number on the raw data form under "CRUC_NO". Oven dry the crucible plus sample overnight at 105 °C for mineral samples or 60 °C for organic samples.
2. The following morning, remove the crucible from the convection oven and place it in a desiccator for 30 minutes. Weigh the crucible plus sample and record its oven-dry weight under "OD_WT."

3. Carefully place the crucible plus sample in a muffle furnace and secure the door. Set the furnace temperature at 450 °C and turn on the unit. The sample should be left overnight at this temperature.

4. The following morning, turn the furnace off and allow to cool for 30 minutes. Carefully remove the crucible from the furnace and allow to cool in the desiccator with a dish of desiccant.

   NOTE: Because a vacuum may be created when cooling extremely hot samples, extra caution should be exercised when opening the desiccator. If a vacuum has formed, the lid may be extremely hard to remove and/or a rush of air may enter the desiccator upon opening.

5. Weigh the crucible plus remaining soil and record this weight under "ASHED_WT" on the raw data form.

7.7 Calculations

The following calculation may be performed by computer after the raw data are entered. It is advantageous to manually check a few samples using the calculation to understand the procedure and to test the accuracy of the computer program.

$$\text{Percent Organic Matter (OM\_LOI)} = \frac{\text{OD\_WT} - \text{ASHED\_WT}}{\text{OD\_WT} - \text{CRUC\_WT}} \times 100$$

If the calculated organic matter content is 20 percent or more, the sample is assumed to be an organic sample. If any samples which were initially labeled as mineral are determined to have 20 percent or more organic matter, batch these with the organic samples, or vice versa. Report these samples to the QA manager and the soil sampling task leader as soon as possible.

7.8 References

MacDonald, C. C. 1977. *Methods of Soil and Tissue Analysis in the Analytical Laboratory.* Maritimes Forest Research Centre Information Report, M-X-78. Fredericton, New Brunswick, Canada.

U.S. Department of Agriculture/Soil Conservation Service. 1975. *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Survey.* Agriculture Handbook No. 436, U.S. Department of Agriculture, U.S. Government Printing Office, Washington, D.C. 754 pp.

8.0 Air-Dry Moisture Determination

8.1 Overview

Air-dry moisture determination is done both at the preparation laboratory and at the analytical laboratory. The procedure for assessing air-dry moisture is not to be performed, however, until the soil is believed to be air dry (see Section 4.6.1). In the preparation laboratory, the process is used to ensure that each sample is at an acceptable moisture level for further processing. In the analytical laboratory, the air-dry moisture is determined on all samples to convert all results to an oven-dry basis, and if specified in a procedure, to calculate the weight of sample equivalent to a given weight of oven-dry soil (Brady, 1974).

8.1.1 Summary of Method

A subsample of the air-dried bulk soil sample is weighed, oven-dried for approximately 24 hours, and reweighed. The initial and final weights are used to calculate a percent weight loss.

8.1.2 Interferences

Sample weights can be affected by salts, oils, and moisture present on skin. Losses of fine silt and clay, caused by excessive movement of the samples, will cause erroneously calculated moisture values.

8.1.3 Safety

Forceps or heat-resistant gloves should be used to handle weighing dishes after removal from the oven.

8.2 Sample Collection, Preservation, and Storage

A subsample is taken from the bulk soil sample after it is believed to be fully air-dried. Analysis takes places immediately thereafter; no preservation or storage is required.

8.3 Equipment and Supplies

8.3.1 Apparatus

1. Balance, capable of weighing to 0.01 g.

2. Convection oven.

3. Desiccator and desiccant.

4. Forceps or finger cots.

5. Thermometer, 0 °C to 200 °C range.

6. Weighing containers capable of withstanding intermittent heating to 110 °C and cooling to room temperature (analytical laboratory).

7. Balance calibration weights, 3-5 weights covering expected range.

8.3.2 Consumable Materials

1. Aluminum weighing dishes, pre-numbered (preparation laboratory).

2. Aluminum weighing pans, disposable (analytical laboratory).

3. Gloves, unpowdered.

4. Air-dry moisture raw data forms (Appendix B, Figure B-8) (preparation laboratory) and air-dry moisture log book (analytical laboratory).

5. Form 1, air-dry moisture percent, and Form QC-1 (Appendix B, figures B-9 and B-10, respectively).

8.4 Calibration and Standardization

The calibration of the balance is described in Appendix A, General Laboratory Procedures. The thermometers should be checked periodically to ensure that they are measuring temperature accurately. The oven should be monitored to ensure that temperature fluctuation does not exceed ±5 °C.

8.5 Quality Control

NOTE: Analytical laboratory quality control (QC) results are recorded on Form QC-1 (Appendix B, Figure B-10). Refer to Section 3.2 for additional information concerning these internal QC checks.

Replicates--One sample from each batch should be analyzed in duplicate. The percent relative standard deviation (%RSD) should be 15 percent or less.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy window provided by the quality assurance (QA) manager.

8.6 Procedure

8.6.1 Preparation Laboratory

NOTE: Data for this procedure are recorded on the air-dry moisture raw data form (see Appendix B, Figure B-8). Once a soil sample is determined to be air dry, the information is also entered on the bulk sample processing raw data form (Appendix B, Figure B-3).

1. Thoroughly mix the *air-dry sample* with gloved hands. Transfer a subsample of approximately 15 g into a pre-numbered aluminum weighing dish of known weight. Enter the dish number on the air-dry moisture raw data form under "TIN_NO." Handle the weighing dish with forceps or finger cots.

NOTE: Because the aluminum weighing dishes are manufactured to be a nearly-constant weight, the average weight of ten labeled aluminum weighing dishes may be used.

2. Weigh the dish plus sample to the nearest 0.01 g and record this initial weight under "INIT_WT." Place the dish in a convection oven which has equilibrated at 105 °C for mineral samples or 60 °C for organic samples. Allow the sample to oven dry overnight at this temperature.

3. The following morning, remove the sample from the oven and allow to cool for 30 minutes in a desiccator. Weigh the dish plus sample to the nearest 0.01 g and record this oven-dry weight under "OD_WT."

8.6.2 Analytical Laboratory

NOTE: Data for this procedure are recorded on Form 1 oven dried moisture percent (Appendix B, Figure B-9). Figures within the square brackets, [ ], represent the form number and column in which the data are recorded.

1. Allow oven to equilibrate at the required temperature ±5 °C for at least 24 hours. Heat the oven to 105 °C for mineral soils; 60 °C for organic soils.

2. Tare each weighing pan to the nearest 0.01 g and note this value for future calculations.

3. Weigh 10.00 g of mineral soil or 6.00 g of organic soil and record the exact air-dry weight [1-B].

4. Dry soils for 24 hours.

5. Remove weighing pan from oven; allow soil to cool in a desiccator. Weight each sample to ±0.01 g and record oven-dry weight [1-C].

8.7 Calculations

8.7.1 Preparation Laboratory

The following calculations may be performed by computer. It is advantageous to manually check a few samples using these calculations to understand the procedure and to test the accuracy of the computer program.

$$\text{Percent air-dry moisture (MOIST\_P)} = \frac{\text{INIT\_WT} - \text{OD\_WT}}{\text{OD\_WT} - \text{TIN\_WT}} \times 100$$

If the calculated moisture content is above 2.5 percent for mineral soils or above 6.0 percent for organic soils, allow the bulk sample to continue air-drying and repeat the procedure at a later time. However, if the sample is below the cutoff percent moisture content for the soil type, then the air-dry sample may be rebagged and placed in cold storage or it may immediately undergo the next stage of processing.

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8.7.2 Analytical Laboratory

NOTE: Designations within the square brackets, [ ], represent the form number and column in which the data are recorded on Form 1 (Appendix B, Figure B-9).

Percent moisture = ([Air-dry wt. - Oven-dry wt.] ÷ Oven-dry wt.) × 100

MOIST [1-D] = ([1-B] - [1-C]) ÷ [1-C] × 100

8.8 References

Brady, N.C. (ed.). 1974. *The Nature and Property of Soils.* Eighth Edition. MacMillan Publishing Co., Inc., New York, New York.

9.0 Particle Size Analysis

9.1 Overview

Particle size analysis is determined on the less than 2-mm fraction from mineral horizons only. The sieve/pipet/gravimetric method described in *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples* (USDA/SCS, 1984) is used.

9.1.1 Summary of Method

Organic matter is removed from the sample by digestion with hydrogen peroxide. The sand fractions are separated from the silt and clay fractions by wet sieving. The silt and clay fractions are suspended in water; aliquots taken from the suspension under specified conditions are dried and then weighed. The sand fractions are sieved and each fraction is weighed. The resulting gravimetric data allow calculation of the percentage of each particle size class.

9.1.2 Interferences

While the soil in suspension is settling, the graduated cylinders containing the suspension cannot be disturbed, nor can the temperature vary. Foam insulation, a constant temperature water bath, or temperature-controlled room may be used to maintain constant temperature. When handling weighing bottles, use forceps, finger cots, cotton gloves, or vinyl gloves to avoid adding weight from moisture and from body salts and oils.

9.1.3 Safety

Forceps or heat-resistant gloves should be used to handle weighing bottles after removal from the oven. Use waterproof gloves while handling hydrogen peroxide. Wear protective clothing and safety glasses when handling reagents or operating instruments.

9.2 Sample Collection, Preservation, and Storage

The subsamples for particle size analysis are taken from the bulk soil sample after it has been air dried, homogenized, and tested for moisture content (see sections 4.0 and 8.0). Samples should be stored at 4 °C until ready for analysis.

9.3 Equipment and Supplies

9.3.1 Apparatus

1. Fleaker, Erlenmeyer flask, or other suitable container, 250-mL or equivalent (tare to ±0.1 mg).
2. Pasteur-Chamberlain filter candles (or equivalent), fineness "F"; store in double-deionized water.
3. Reciprocating shaker, 120 oscillations per minute.
4. Sedimentation cylinders (1-L graduated cylinders, optional).

5. Stirrer, motor-driven.

6. Stirrer, hand--Fasten a circular piece of perforated plastic to one end of a brass rod.

7. Shaw pipet rack or equivalent.

8. Pipets, 25-mL, automatic (Lowry with overflow bulb or equivalent).

9. Polyurethane foam pipe-insulation, constant temperature bath (±1 °C), or temperature-controlled room (±1 °C).

10. Sieve shaker, 1.25-cm vertical and lateral movement, and 500 oscillations per minute, or equivalent. Unit must accommodate a nest of sieves.

11. Glass weighing bottles, 90-mL, wide-mouth with screw caps, or equivalent, (tare to ±0.1 mg), capable of withstanding intermittent heating to 110 °C and cooling to room temperature.

12. Balance, top-loading, capable of weighing to 0.01 g.

13. Balance, analytical, capable of weighing to 0.0001 g.

14. Set of sieves, square-mesh, woven phosphor-bronze or stainless steel wire cloth; U.S. Series and Tyler Screen Scale equivalent designations as follows:

Nominal Opening (mm)	U.S. No.	Tyler Mesh Size
1.0	18	16
0.5	35	32
0.25	60	60
0.105	140	150
0.046	300	300

15. Receiving pan, used with sieves.

16. Hot plate (block digester, optional).

17. Thermometer, range 10 to 50 °C.

18. Evaporating dishes, or equivalent, 125- or 250-mL.

19. Desiccator and desiccant.

20. Watch glass.

21. Convection oven.

22. Clamp and ring stand.

23. Stoppers (optional).

24. Stop watch.

9.3.2 Reagents and Consumable Materials

1. Hydrogen peroxide (H_2O_2), 30 to 35 percent.

2. Sodium carbonate (Na_2CO_3).

3. Sodium hexametaphosphate [$(NaPO_3)_6$], dispersing agent--Dissolve 35.7 grams of $(NaPO_3)_6$ and 7.94 grams of Na_2CO_3 in deionized (DI) water and dilute to 1 L.

4. Phosphorus pentoxide (P_2O_5)--Used as desiccant.

5. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

6. Kimwipes.

7. Forms--Form 2 particle size parameters raw data, Form 3 particle size parameters calculated data, Form QC-2, and Form QC-3 (Appendix B, figures B-11 through B-14, respectively).

9.4 Calibration and Standardization

Periodically check thermometers against an NBS-certified standard to ensure that they are measuring temperature accurately. Temperatures of the suspensions should vary no more than ±1 °C.

Calibration of the balance is described in Appendix A, General Laboratory Procedures.

9.5 Quality Control

NOTE: Log all QC data on Forms QC-2 and QC-3 (Appendix B, figures B-13 and B-14); refer to Section 3.2 for additional information concerning these internal QC checks.

Reagent Blanks--A 25-mL aliquot of the diluted dispersion solution (10.0 mL of the hexametaphosphate dispersion solution diluted to 1 L), dried and weighed, is used as the clay reagent blank. One blank should be analyzed with each batch.

Replicates--One sample from each batch should be analyzed in duplicate. The percent relative standard deviation (% RSD) should meet the limits in Table 3-1.

Quality Control Check Standard (QCCS) -- A well-characterized soil having a minimum of 5 percent each of sand, silt, and clay is analyzed with each batch of soils. This QCCS standard is analyzed at least once with each group of soils. For example, if the analytical laboratory has eight sets of sedimentation cylinders-stirrers-pipets, one of these sets would be used for the QCCS sample with every seven or fewer soil samples. Although data for all fractions are reported on Form QC-2 and QC-3, only the *total* sand, silt, and clay fractions are subjected to the criterion that the percent relative standard deviation (%RSD) between measured and known values is 10 percent or less.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy window provided by the quality assurance (QA) manager.

9.6 Procedure

NOTE: Figures within the square brackets, [ ], represent the form number and column in which the data are entered on forms 2 and 3, particle size parameters, raw data and calculated data, respectively (Appendix B, figures B-11 and B-12).

9.6.1 Removing Organic Matter

1. Weigh 10.00 g air-dried soil into a tared (to the nearest 0.01 g) Fleaker or equivalent and record this value [2-B]. For soils low in clay, it may be necessary to double the amount of soil to meet the required precision. Doubling the amount of soil does not require any adjustments to the remaining steps in this procedure.

2. Add 50 mL of DI water followed by 5 mL of H_2O_2. Cover the Fleaker with a watch glass to avoid sample loss. If a violent reaction occurs, repeat the H_2O_2 treatment periodically until no more foaming occurs.

NOTE: If foaming results in sample loss, repeat from Step 1.

3. Heat the Fleaker to about 90 °C on an electric hot plate. Add H_2O_2 in 5-mL quantities at 45-minute intervals until the organic matter is destroyed, as determined visually by a lack of effervescence. Continue heating for about 30 minutes to remove excess H_2O_2.

NOTE: For simplicity, use block digestion apparatus, if available, and replace Fleakers with block digester tubes. The removal of the organic matter may require 24 to 36 hours.

4. Place the Fleaker in a rack and add about 150 mL of DI water in a jet strong enough to stir the sample well. Remove solution from the suspension with a filter-candle system. Five such washings and filterings are usually sufficient; soils containing much coarse gypsum may require additional treatments.

5. Remove soil that adheres to the filter by applying gentle air pressure.

6. Dry the sample overnight in an oven at 105 °C, cool the sample in a desiccator, and weigh the H_2O_2-treated sample plus Fleaker to the nearest 0.01 g and record the soil weight [2-C]. Use the weight of the oven-dry, H_2O_2-treated sample as the weight for calculating percentages of the particle-size fractions.

9.6.2 Separating Sand from Silt and Clay

1. Add 10 mL of sodium hexametaphosphate dispersing agent (see Section 9.3.2, Step 3) to the Fleaker that contains the oven-dry treated sample. Bring the volume to approximately 200 mL. Stopper the Fleaker and shake overnight on a horizontal reciprocating shaker at 120 oscillations per minute.

2. Place a 300-mesh sieve on top of the sedimentation cylinder. A clamp and ring stand may be used to hold the sieve in place. Wash the dispersed sample onto the sieve with DI water. Avoid using jets of water because they may break the fine mesh of the sieve.

Fine silt and clay will pass through the sieve into the cylinder. The sand and some coarse silt will remain on the sieve. It is important to wash all particles of less than 0.02-mm diameter through the sieve. Gently tapping the sieve clamp with the side of the hand will facilitate sieving.

3. Continue washing the sand until the suspension volume in the cylinder is about 800 mL.
4. Remove the sieve from the cylinder. Wash the sand into a tared evaporating dish or original Fleaker with DI water. Dry the sand overnight at 105 °C. Continue to Section 9.6.3 for fractionation of the sand.
5. Dilute the silt and clay suspension in the cylinder to 1.00 L with DI water. Cover the cylinder with a watch glass. Continue to Section 9.6.4 for the separation of the fine silt and clay.

9.6.3 Sieving and Weighing the Sand Fractions

1. Weigh the total dry sand (from 9.6.2, Step 4) to the nearest 0.01 g and record [2-D].
2. Stack sieves (tared to the nearest 0.01 g) from largest opening (1.0 mm) to smallest nominal opening with the 1.0 mm sieve on the top and the receiving pan on the bottom.
3. Quantitatively transfer the dried sand to the top sieve.
4. Cover and secure the stack of sieves and shake for 3 minutes.
5. Weigh the sand fraction retained by each sieve to nearest 0.01 g and record; [2-E] very coarse; [2-F] coarse, [2-G] medium; [2-H] fine; [2-I] very fine.

9.6.4 Pipetting

All pipetting must be performed in a location free from drafts and temperature fluctuations. A temperature-controlled room, constant-temperature water bath, or foam insulation may be used.

1. Allow 12 to 24 hours for the temperature of suspension to equilibrate.
2. Stir the material in the sedimentation cylinder for 6 minutes with the motor-driven stirrer. Stir 8 minutes if suspension has been standing for more than 16 hours.

   If stoppers of adequate size are available, it is preferable to stopper the cylinder, invert, and swirl. Care must be taken to ensure that the stopper is held tightly in the cylinder. Repeat this procedure at least six times. Inspect the bottom and sides of the cylinder to ensure that fine particles are not adhering to the glass walls of the cylinder.
3. Remove the stirrer and either (1) cover the cylinder with a length of polyurethane foam pipe-insulation, (2) immerse the cylinder in a constant-temperature water bath, or (3) place the cylinder in a temperature-controlled room.
4. Stir the suspension for 30 seconds with a hand stirrer; use an up-and-down motion. Record the time when the stirring is complete. Do not move, stir, or otherwise disturb the cylinder from this point until all pipetting has been completed.

5. Take the temperature of the solution in the cylinder by gently lowering a thermometer 5 cm into the suspension. Support the thermometer with a clamp to reduce disturbance to the suspension.

6. Use the temperature and Table 9-1 to determine the settling time required for the <0.02-mm fraction, e.g., at 22 °C allow 4 minutes, 35 seconds.

Table 9-1. Sedimentation Times for Fine Silt and Clay Particles Settling Through Water to a Depth of Ten Centimeters

	Settling Time with Indicated Particle Diameter[a]	
Temperature °C	≤0.002 mm hr:min	≤0.02 mm min:sec
20	8:00	4:48
21	7:49	4:41
22	7:38	4:35
23	7:27	4:28
24	7:17	4:22
25	7:07	4:16
26	6:57	4:10
27	6:48	4:04
28	6:39	4:00
29	6:31	3:55
30	6:22	3:49
31	6:14	3:44

[a] Values calculated from Stokes' equations, assuming a particle density of 2.65 g/cm^3. This figure for particle density is arbitrary and has been chosen to satisfy simultaneously the two definitions of the clay fraction, i.e., particles that have an effective diameter of 0.002 mm or less and particles that have a settling velocity of 10 cm in 8 hours at 20 °C.

7. Approximately 60 seconds before the sedimentation time has elapsed, slowly lower the Lowry automatic pipet 10 cm into the suspension. (A 25-mL volumetric pipet premarked for a 10-cm depth and clamped firmly in place on a stand may be used.)

8. At the appropriate time, slowly (allow about 12 seconds) fill the pipet. Carefully remove it from the suspension.

9. Wipe clean the outside of the pipet and empty the contents into a drying container, such as a 90-mL widemouth bottle, tared to the nearest 0.1 mg. Rinse the pipet into the bottle once with DI water (add the rinse water to the contents of the bottle).

10. Dry the bottle and contents in an oven overnight at 105 °C. Cool in a desiccator over phosphorus pentoxide (P_2O_5). Weigh to nearest 0.1 mg and record net weight [2-J] to nearest 0.1 mg.

11. Repeat steps 5 through 10 for the <0.002-mm clay fraction. The <0.002-mm fraction may be pipetted at a time between 5 and 8 hours depending on the temperature and the table used. The use of Table 9-1 and a depth of 10 cm is strongly recommended and is the easiest method. Table 9-2 should be used only when time constraints necessitate. Weigh dried material and record net weight [2-K] to nearest 0.1 mg.

Table 9-2. Sedimentation Times and Pipetting Depths for Clay Particles

	Sedimentation Time[a]			
Temperature °C	5 hr.	5 hr. 30 min.	6 hr.	6 hr. 30 min.
	Pipetting Depth (cm)			
20.0	6.44	7.08	7.72	8.37
20.5	6.52	7.17	7.82	8.47
21.0	6.59	7.25	7.91	8.57
21.5	6.68	7.34	8.01	8.68
22.0	6.75	7.43	8.11	8.78
22.5	6.88	7.54	8.21	8.88
23.0	6.91	7.60	8.30	8.98
23.5	6.98	7.69	8.39	9.09
24.0	7.08	7.78	8.49	9.20
24.5	7.15	7.86	8.59	9.30
25.0	7.24	7.96	8.69	9.41
25.5	7.31	8.05	8.78	9.51
26.0	7.40	8.14	8.88	9.62
26.5	7.47	8.22	8.97	9.72
27.0	7.56	8.32	9.08	9.83
27.5	7.64	8.40	9.17	9.93
28.0	7.74	8.51	9.28	10.06
28.5	7.82	8.61	9.39	10.17
29.0	7.91	8.70	9.49	10.28
29.5	7.99	8.79	9.59	10.39
30.0	8.08	8.88	9.69	10.50

[a] Calculations provided by USDA/SCS National Soil Survey Laboratory, Lincoln, Nebraska (personal communication) (assuming a particle density of 2.65 g/cm^3).

9.7 Calculations

NOTE: Designations within the square brackets, [ ], represent the form number and column in which the data are entered on forms 2 and 3, particle size parameters, raw data and calculated data, respectively (Appendix B, figures B-11 and B-12).

9.7.1 Input (raw data)

[2-B] = air-dry sample weight
[2-C] = treated (oven-dry, organic-free) sample weight
[2-D] = oven-dry net weight of total sand
[2-E] = oven-dry net weight of very coarse sand
[2-F] = oven-dry net weight of coarse sand
[2-G] = oven-dry net weight of medium sand
[2-H] = oven-dry net weight of fine sand
[2-I] = oven-dry net weight of very fine sand
[2-J] = oven-dry net weight of first pipet
[2-K] = oven-dry net weight of second pipet
RBLK1 = weight of clay reagent blank

9.7.2 Calculated Data

All calculations are made to the nearest 0.1 weight percent.

SAND [3-B] = ([2-E] + [2-F] + [2-G] + [2-H] + [2-I]) ÷ [2-C] × 100

SILT [3-C] = 100 − ([3-B] + [3-D])

CLAY [3-D] = ([2-K] − RBLK1) ÷ [2-C] × (1000 ÷ 25) × 100

VC_SAND [3-E] = [2-E] ÷ [2-C] × 100

C_SAND [3-F] = [2-F] ÷ [2-C] × 100

M_SAND [3-G] = [2-G] ÷ [2-C] × 100

F_SAND [3-H] = [2-H] ÷ [2-C] × 100

VF_SAND [3-I] = [2-I] ÷ [2-C] × 100

C_SILT [3-J] = [3-C] − [3-K]

F_SILT [3-K] = ([2-J] − [2-K]) ÷ [2-C] × (1000 ÷ 25) × 100

9.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standard Specification for Reagent Water*, D-1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

U.S. Department of Agriculture/Soil Conservation Service. 1984. *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples.* Soil Survey Investigations Report No. 1, U.S. Government Printing Office, Washington, D.C.

10.0 pH Determination

10.1 Overview

The pH is defined as the negative logarithm of the activity of hydrogen ions (H^+). The H^+ activity is a measure of the "effective" concentration of hydrogen ions in solution; it is always equal to or less than the true concentration of hydrogen ions in solution. Values range from pH 1 to pH 14, with pH 1 most acidic, pH 7 neutral (at 25 °C), and pH 14 most alkaline. Each pH unit represents a tenfold change in H^+ activity (i.e., a pH 4 solution is 10 times more acidic than a pH 5 solution).

When the pH of a sample solution is measured, the hydrogen ions come into equilibrium with the ion exchange surface (glass) of a calibrated pH electrode, which creates an electrical potential. This voltage difference is measured by the pH meter in millivolts (mv), which is then converted and displayed as pH units.

10.1.1 Scope and Application

The following procedure was developed to standardize the measurement of pH in soils. The method has been written assuming that the Orion Model 611 pH meter and an Orion Ross combination pH electrode are used (Orion, 1983). The method, however, can be modified for use with other instrumentation meeting specifications equivalent to those given in Section 10.3.1.

The applicable pH range for soil solutions is 3.0 to 11.0.

10.1.2 Summary of Method

Two suspensions of each soil sample are prepared, one in deionized (DI) water and one in 0.01 M calcium chloride ($CaCl_2$). The pH of each suspension is measured with a pH meter and a combination electrode. This method is modified from USDA/SCS (1984). The DI water pH is generally higher than the 0.01 M $CaCl_2$ pH.

10.1.3 Interferences

Factors that normally affect the measurement of pH are (1) electrolyte content of the extractant; (2) soil-to-solution ratio; (3) temperature and CO_2 content of the extractant; (4) errors that occur with instrument calibration, standard preparation, and liquid junction potential; (5) organic and inorganic constituents; (6) length of time the soil and solution stand before they are measured; and (7) technique used in reading the sample suspension.

Soils high in salts, especially sodium, may interfere with the pH reading and the electrode response time. Clay particles may clog the liquid junction of the pH reference electrode, slowing the electrode response time; thoroughly rinse the electrode with DI water between sample readings to avoid this problem. Wiping the electrode dry with cloth, laboratory tissue, or similar materials or removing the electrode from solution when the meter is not on standby may cause electrode polarization.

The initial pH of a nonalkaline soil will usually be as much as 0.5 pH unit greater than the pH taken after the sample has set for 30 minutes or longer. The pH can vary as much as 1.0 pH unit between the supernatant and soil sediment. Always place the electrode junction at the same distance (approximately 3 mm) above the surface of the soil sediment to maintain uniformity in pH readings.

10.1.4 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids should be restricted to a fume hood.

10.2 Sample Collection, Preservation, and Storage

The subsamples for pH measurement are taken from the bulk soil sample after it has been air dried, homogenized, and tested for moisture content (see sections 4.0 and 8.0). Samples should be stored at 4 °C until ready for analysis. Preparation of the soil suspensions for pH measurement is described in Section 10.6.1.

10.3 Equipment and Supplies

10.3.1 Equipment Specifications

1. Digital pH/mV meter, capable of measuring pH to ±0.01 pH unit, potential to ±1 mV, and temperature to ±0.5 °C. The meter must also have automatic temperature compensation capability (Orion Model 611 or equivalent).

2. A combination pH electrode, made of high quality, low-sodium glass. At least two electrodes, one as a backup, should be available. Gel-type reference electrodes must *not* be used; an Orion Ross combination pH electrode or equivalent with a retractable sleeve is recommended.

3. Balance, capable of weighing to ±0.001 g.

4. Balance calibration weights, 3-5 weights covering expected range.

10.3.2 Reagents

1. pH Calibration Buffers (pH 4.0 and 7.0)--Commercially available pH calibration buffers (National Bureau of Standards [NBS]-traceable) at pH values of 4.0 and 7.0 (two sets from different sources for calibration and quality control checks).

2. Buffer of pH 4.0 for quality control check standard (QCCS)--The QCCS can be purchased or it can be prepared from 0.05 M potassium hydrogen phthalate ($KHC_8H_4O_4$ or KHP). This buffer must be from a different container or lot than the NBS-traceable standards used for electrode calibration. Dry KHP for 2 hours at 110 °C, cool to room temperature in a desiccator. Weigh 10.21 g of KHP, dissolve it in DI water, and dilute the solution to 1.00 L. To preserve the KHP solution, add 1.0 mL of chloroform or one crystal (about 10 mm in diameter) of thymol per liter of the buffer solution. This solution has the following pH values at the temperatures given: 3.99 at 15 °C; 4.002 at 20 °C; 4.008 at 25 °C; and 4.015 at 30 °C.

3. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

4. Calcium hydroxide [$Ca(OH)_2$]--Dissolve 0.185 g $Ca(OH)_2$ in DI water and dilute to 1 L.

5. Hydrochloric acid (HCl)--Dilute 1 mL concentrated HCl to 1 L with DI water.

6. Stock calcium chloride solution ($CaCl_2$), 1.0 M--Dissolve 55.49 g of anhydrous $CaCl_2$ or 73.51 g of $CaCl_2 \cdot 2H_2O$ in DI water and dilute to 500 mL.

7. Calcium chloride, 0.01 M $CaCl_2$--Dilute 20 mL of stock 1.0 M $CaCl_2$ to 2.0 L with DI water. If the pH of this solution is not between 5 and 6.5, adjust the pH by addition of dilute $Ca(OH)_2$ or HCl, as needed.

8. Potassium chloride (3 M)--Dissolve 224 g KCl in DI water and dilute to 1 L.

9. Potassium chloride (0.1 M).

10. Sodium hydroxide (NaOH) pellets.

10.3.3 Consumable Materials

1. Beakers, plastic, or paper containers, 50-mL.

2. Glass stirring rods or disposable stirrers, one per sample.

3. Weighing pans, disposable.

4. Forms--Form 4 pH in water, Form 5 pH in 0.01 M calcium chloride, Form QC-4, and Form QC-5 (Appendix B, figures B-15 through B-18, respectively).

10.4 Calibration and Standardization

NOTE: For storage and readings, the electrode need only be immersed to cover the liquid junction of the reference electrode (typically about 3 mm). Rinse the electrode with DI water between each sample and each buffer to prevent solution carryover. Do not rub or blot electrode dry because this may produce a static electric charge and thereby polarize the electrode.

10.4.1 Instrument Preparation

1. Plug in the instrument and verify that the control knob is on "STD BY." Allow at least 30 minutes for instrument warm-up prior to use.

   NOTE: If instrument is used frequently, leave on and in "STD BY" mode between uses.

2. Connect the combination electrode to the meter. Consult the pH electrode manual for the proper procedure.

3. Verify that the level of reference filling solution (3 M KCl) in the electrode is just below the fill hole and that the fill hole is uncovered during measurement (slide the plastic sleeve down).

4. Calibrate the meter for temperature weekly using a two-point standardization (one point at approximately 5 °C to 10 °C and the other point at room temperature).

   a. Room temperature--Place the electrode and an NBS-traceable thermometer into DI water which is at room temperature. Swirl the electrode for 5 to 10 seconds.

   b. Turn the knob on the meter to "TEMP." Using a small screwdriver, turn the "TEMP ADJ" screw on back of the pH meter to adjust the display to the temperature reading of the thermometer.

   c. Cold temperature--Place the probe and the NBS-traceable thermometer into a 250-mL beaker containing cold DI water (5 to 10 °C). Repeat Step b by adjusting the display with the "TEMP Slope" screw on the back of the meter.

   d. Continue steps a through c until no further adjustments are necessary and record all values in the logbook.

10.4.2 Calibration with Buffers

1. Check the meter temperature calibration daily with a beaker of room temperature DI water and an NBS-traceable thermometer. If the display differs from the NBS-traceable thermometer by more than 1.0 °C, complete adjustments as described in Section 10.4.1, above.

2. Pour fresh pH 7.00 and pH 4.00 buffer solutions into labeled 50-mL beakers (one "RINSE", one "CALIBRATION", and one "CHECK" beaker for each buffer). Rinse all beakers three times with buffer solutions and fill with the appropriate buffer solutions.

3. Rinse the electrode with DI water. Place the electrode into the pH 7.00 "RINSE" beaker and swirl for 40 seconds. Place the electrode into the "CALIBRATION" beaker, turn the knob to "pH", swirl for 30 to 60 seconds (or until the pH reading is stable), and read the value on the display. Consult the pH-temperature chart, Table 10-1. Use the "CALIBRATE" knob to adjust the pH reading on the meter to the theoretical pH of the buffer solution at the appropriate temperature.

4. Repeat Step 3 for pH 4.00 buffer using the "% SLOPE" knob to adjust the pH reading.

5. Repeat steps 3 and 4 until both the pH 7.00 and the pH 4.00 buffers agree with the theoretical pH of the buffer solution at the appropriate temperature.

6. Check the standardization using the buffer solutions in the "CHECK" beakers. If the values differ by more than ±0.03 units from the theoretical value, repeat the standardization process. When the meter standardization is acceptable, record the pH and temperature readings for each buffer solution in the pH logbook.

10.4.3 Maintenance

1. Weekly, drain the 3 M KCl filling solution from the electrode using a disposable pipet with Teflon tubing attached.

2. Refill the electrode chamber with the 3 M KCl filling solution and rinse by inverting the electrode. Drain the solution as in Step 1.

Table 10-1. pH Values of Buffers at Various Temperatures

Temperature						
25 °C	0 °C	5 °C	10 °C	20 °C	30 °C	40 °C
1.68	1.67	1.67	1.67	1.67	1.68	1.69
3.78	3.86	3.84	3.82	3.79	3.77	3.75
4.01	4.00	4.00	4.00	4.00	4.02	4.03
6.86	6.98	6.95	6.92	6.87	6.85	6.84
7.00	7.11	7.08	7.06	7.01	6.98	6.97
7.41	7.53	7.50	7.47	7.43	7.40	7.38
9.18	9.46	9.40	9.33	9.23	9.14	9.07
10.01	10.32	10.25	10.18	10.06	9.97	9.89

3. Refill the electrode with the filling solution to just below the fill hole.

4. Gently spin the electrode overhead for approximately 1 minute by the leader to remove any air bubbles. Be careful to stand clear of any obstacles when swinging the electrode.

10.4.4 pH Meter Electronic Checkout

NOTE: This procedure should be performed whenever a new pH meter is set up or when calibration problems occur.

1. Connect the shorting strap as outlined in the Orion pH meter manual.

2. Turn the "TEMP ADJ" and "TEMP SLOPE" screws fully counterclockwise and record the display pH value (turn knob to "pH" position).

3. Turn the "TEMP SLOPE" screw 7.5 turns clockwise and record the display pH value. The difference between the "TEMP SLOPE" value in Step 2 and Step 3 should be between 7.0 and 15.0.

4. Turn the "TEMP ADJ" screw until a value between 50.0 ± 0.1 appears on display.

5. Press the test button. A value of 42.2 ± 2.0 should appear on the display when the knob is in the "TEMP" position. If this value is not displayed, keep depressing the test button and use the "TEMP SLOPE" screw to adjust the reading to 4.0 ± 1.0. Release the test button and use the "TEMP ADJ" screw to obtain a reading of 50.0 ± 0.1. Press the test button again.

The reading should be 42.2 ± 2.0. Repeat this procedure several times if the value is not in range.

10.4.5 Electrode Etching Procedure

The electrode etching procedure is described in Section 6.4.5.

10.5 Quality Control

Log all quality control (QC) data on forms QC-4 and QC-5 (Appendix B, figures B-17 and B-18); refer to Section 3 for additional information concerning these internal quality control checks.

Reagent Blanks--Analyze one blank of each suspension solution. The blank used for each pH method is the reagent used: DI water or 0.01 M $CaCl_2$. The measured pH of each blank should fall between 4.5 and 7.5 pH units.

Replicates--One sample from each batch should be analyzed in triplicate for pH in each of the DI water and 0.01 M $CaCl_2$ solutions. The standard deviation for each set of three replicates should be 0.10 pH units or less.

Quality Control Check Sample (QCCS)--A pH 4.00 standard from a different preparation source or lot number than that used for the calibration is used as the QCCS. Analyze a QCCS before beginning analysis of routine samples, at specified intervals thereafter, e.g., after every ten samples and after completion of routine sample analysis for the day. Measured values of each QCCS should be 4.00 ± 0.05. If the QCCS does not meet this criterion, recalibrate the electrode and repeat the QCCS measurement using a fresh QCCS. If acceptable results still cannot be obtained: check electrode for clean reference junction, check wiring straps into meter, check for static electricity, and check to see if enough filling solution is contained within the electrode. If a problem still persists, replace electrode or meter, or both.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy window provided by the quality assurance (QA) manager.

10.6 Procedure

NOTE: The figures in the square brackets, [ ], represent the column of the appropriate form where the data are recorded.

10.6.1 Preparing Soil Suspensions

1. Weigh 20.0 g of air-dry mineral soil into a beaker and add 20.0 mL of DI water; for organic soils, use 5.0 g of soil and 25.0 mL of DI water. Log exact sample weight [4-B] and volume [4-C].
2. Allow soil to absorb the liquid without stirring.
3. Stir the mixture for 10 seconds and allow mixture to sit for 15 minutes.
4. Repeat Step 3 three times.

5. Repeat steps 1 through 4, replacing the DI water with 0.01 M $CaCl_2$. Log sample weight [5-B] and volume of 0.01 M $CaCl_2$ [5-C].

10.6.2 pH Measurements

1. After the final stirring, allow the suspension to settle for at least 1 minute. Place the pH electrode in the supernatant of the soil suspension.

   For mineral soils, the reference junction should be below the solution surface and above the soil-solution interface.

   Some organic soils swell upon wetting, so there is no free water available. As long as the reference junction is below the surface of the organic material, an acceptable, repeatable reading generally is attained. When the reading is stable, record pH to the nearest 0.01 pH unit.

2. Report the pH of the soil:DI water suspension, [4-D] and the soil:0.01 M $CaCl_2$ suspension [5-D], for each sample.

3. After measurements are completed, store the electrode in 0.1 M KCl storage solution. Do not let the sensing element and reference junction dry out. The level of the storage solution should be one inch below the filling solution level to prevent influx of the storage solution. Check periodically that the electrode reservoir is full of filling solution.

10.7 Calculations

No calculations are required to obtain pH values. Replicate measurements of the same sample or of duplicate samples should not be averaged.

10.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards Vol. 11.01, Standard Specification for Reagent Water,* D-1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Orion Research Incorporated. 1983. *Institutional Manual - Model 611 pH/millivolt meter.* Orion, Cambridge, Massachusetts.

U.S. Department of Agriculture/Soil Conservation Service. 1984. *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples.* Soil Survey Investigations Report No. 1, U.S. Department of Agriculture, U.S. Government Printing Office, Washington, D.C.

11. Cation Exchange Capacity

11.1 Overview

Cation exchange capacity (CEC), usually expressed in milliequivalents (meq) per 100 g of soil, is a measure of the quantity of readily exchangeable cations neutralizing negative charge in the soil (Rhoades, 1982). Negative charge in the soil can be derived from several sources which fall into two categories: permanent and pH dependant (or variable) charge. Permanent charge sites are the result of isomorphic substitution within the crystal structure of the layer silicate minerals which are commonly thought of as clay minerals. Permant charge CEC is independent of pH, electrolyte concentrations, ion valences and the dielectric constant of the medium which influence the contribution of the overall CEC from the pH dependant charges. The pH dependant CEC is derived from broken bonds at mineral edges, dissociation of acidic functional groups in organic matter and sesquioxides present in the soil, and preferential adsorption of certain ions on the charged particle surfaces. In general, as the pH electrolyte concentration, dielectric constant of the medium, and the ion valences increase, the net contribution of pH dependant charge to the overall CEC increases.

A close approximation of the CEC can be made by the summation of the exchangeable base cations of Ca^{2+}, Mg^{2+}, Na^+, and K^+ and the exchangeable acidity as determined by $BaCl_2$-TEA extraction or the addition of exchangeable Al extracted by KCl (USDA/SCS, 1972).

11.1.1 Scope and Application

Two saturating solutions are used for CEC determination. Ammonium acetate (1.0 N NH_4OAc) buffered at pH 7.0 yields a CEC which is close to the total cation exchange capacity for a specific soil. This saturating solution is commonly used for soil comparisons. In acid soils, this estimate results in a high CEC value because of adsorption of NH_4^+ ions to the pH-dependent exchange sites that exist above the soil's natural pH level. The overestimation will not occur when an unbuffered saturating solution of ammonium chloride (1.0 N NH_4Cl) is used. The NH_4Cl CEC has been termed "effective" CEC (i.e., that which occurs at field pH and is of greater importance because it is a more realistic estimate of CEC than the total CEC by NH_4OAc). The two saturating solutions are retained for the exchangeable cation determinations (sections 12.0 and 13.0). This method has been written assuming use of a mechanical extractor.

11.1.2 Summary of Method

The soil sample is saturated with NH_4^+ from a solution of NH_4OAc or NH_4Cl. Excess NH_4^+ is removed by ethanol rinses. The NH_4^+ is displaced by Na^+ and is analyzed by one of three methods: automated distillation-titration, manual distillation-automated titration, or ammonium displacement-flow injection analysis. The entire procedure is repeated with a fresh aliquot of sample and a solution of NH_4Cl as the NH_4^+ source. These methods are based on Doxsee (1985), Rhoades (1982), and USDA/SCS (1984).

11.1.3 Interferences

Inconsistency in the NH_4^+ saturating and rinsing steps is the greatest source of error. Soils containing an abundance of minerals, such as biotite and muscovite which may contain inter-lattice NH_4^+, may produce artificially high results. The use of a mechanical extractor minimizes inconsistency.

11.1.4 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids and hydroxide solutions should be restricted to a fume hood.

11.2 Sample Collection, Preservation, and Storage

The subsamples for CEC determination are taken from the bulk soil sample after it has been air dried, homogenized, and tested for moisture content (see sections 4.0 and 8.0). Samples should be stored at 4 °C until ready for analysis. Preparation of the saturating solutions is described in Section 11.3.3.

11.3 Equipment and Supplies

11.3.1 Apparatus for Saturation Procedure

1. Mechanical extractor, 24-place (see Figure 11-1).
2. Reciprocating shaker.
3. Balance, capable of weighing to 0.01 g.
4. Balance calibration weights, 3-5 weights covering expected range.
5. Wash bottle.

11.3.2 Apparatus for Analysis

The apparatus and equipment needed are specific to the selected analytical method. It is not necessary to have equipment for all three analytical methods.

11.3.2.1 Ammonium Displacement-Flow Injection--

1. Flow injection analyzer (FIA), Lachat or equivalent, modified for ammonium chemistry with 630-nm interference filter and consisting of:
   a. Sampler.
   b. Analytical manifold with 200-μL sample loop.
   c. In-line heater.
   d. Colorimeter equipped with a 10-mm flow cell.
   e. Printer.
2. Balance, capable of weighing to 0.001 g.
3. Balance calibration weights, 3-5 weights covering expected range.

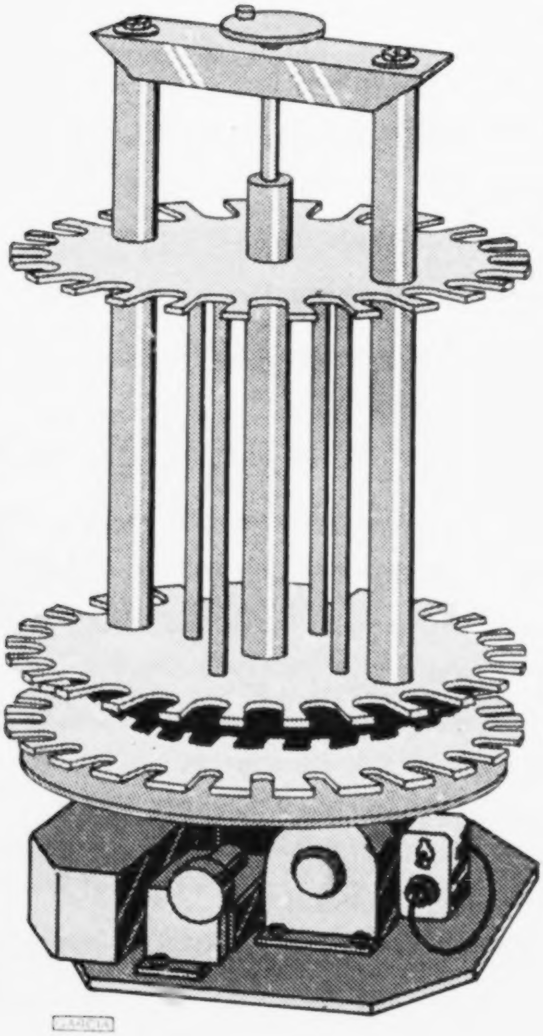

Figure 11-1. Mechanical Extractor.

11.3.2.2 Automated Distillation-Titration--

1. Steam distillation-titration apparatus, Kjeltec Auto 1030 Analyzer, or equivalent.
2. Printer, Alphacom 40, or equivalent.
3. Digestion tubes, 250-mL, straight neck.
4. Balance, capable of weighing to 0.1 g.
5. Balance calibration weights, 3-5 weights covering expected range.
6. Policeman, rubber.

11.3.2.3 Manual Distillation/Automated Titration--

1. Automatic titrator with autosampler, Metrohm or equivalent.
2. Kjeldahl flasks, 800-mL.
3. Balance, capable of weighing to 0.1 g.
4. Balance calibration weights, 3-5 weights covering expected range.
5. Policeman, rubber.

11.3.3 Reagents and Consumable Materials for Saturation Procedure

1. Washed analytical filter pulp, Schleicher and Schuell, No. 289 (see Section 11.6.1 for washing procedure).
2. Glacial acetic acid ($HC_2H_3O_2$).
3. Ammonium hydroxide (NH_4OH), concentrated.
4. Ammonium acetate (NH_4OAc), reagent grade, 1 N, pH 7.0--To 15 L deionized water (DI) in a 20-L bottle, add 1,388 g crystalline ammonium acetate and dissolve by stirring; allow to come to ambient temperature, then dilute to 18 L with DI water; adjust to pH 7.0 with acetic acid or ammonium hydroxide.
5. Ammonium chloride (NH_4Cl), reagent grade, 1 N--Dissolve 535 g in DI water and dilute to 10 L.
6. Ethanol (C_2H_5OH), 95 percent, U.S.P.
7. Nessler's reagent--
    a. Add 4.56 g potassium iodide (KI) to 30-mL DI water in a beaker. Add 5.68 g mercuric iodide (HgI_2). Stir until dissolved.
    b. Dissolve 10 g NaOH in 200-mL DI water.

   c. Transfer NaOH solution to 250-mL volumetric flask. Add Hg solution slowly. Dilute to volume and mix thoroughly. Solution should not contain a precipitate. It can be used immediately.

8. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

9. Syringes, disposable, 60-mL polypropylene (use one sample tube, one reservoir tube, and one tared extraction syringe for each sample).

10. Rubber tubing, 1/8 x 1/4 inch (for connecting syringe barrels).

11. Bottles, linear polyethylene (LPE), 25-mL.

12. Tubes, glass, centrifuge or culture, with caps, 25-mL.

13. Weighing pans, disposable.

11.3.4 Reagents and Consumable Materials for Analysis

The reagents and consumable materials needed are specific to the selected analytical procedure. It is not necessary to have the reagents and materials for all three analytical procedures.

11.3.4.1 Ammonium Displacement-Flow Injection Analysis--

The reagents and consumable materials used depend on recommendations of the manufacturer of the FIA and may vary by make and model.

1. Hydrochloric acid, 0.1 N--Purchased or prepared by the following procedure: Add 150 mL concentrated HCl to approximately 15 L DI water, dilute to 18 L. Standardize 0.1 N HCl by titration against dried primary standard grade sodium carbonate to the methyl orange end-point.

2. Nitroferricyanide reagent--Dissolve 40 g potassium sodium tartrate ($KNaC_4H_4O_6$) and 30 g sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) in 500 mL DI water. Add 10 g sodium hydroxide pellets (NaOH). Add 1.5 g sodium nitroferricyanide ($Na_2Fe(CN)_5NO \cdot 2H_2O$), dilute to 1.00 L, and mix well. Store in a dark bottle. Prepare fresh solution monthly.

3. Sodium hypochlorite reagent--Dissolve 20 g sodium hydroxide and 20 g boric acid in 150 mL of DI water. Add 800 mL 5 percent solution NaOCl. Dilute to 1.00 L with DI water. Store in a dark bottle. Prepare fresh solution monthly.

4. Sodium phenate reagent--Dissolve 95 mL of 88 percent liquified phenol in 600 mL DI water. While stirring, slowly add 120 g NaOH. Cool. Add 100 mL ethanol and dilute to 1.00 L. Store in a dark bottle.

5. Nitrogen standard solution, 1,000 mg NH_4-N/L--Dissolve 3.819 g ammonium chloride (NH_4Cl), dried at 105 °C, in DI water and dilute to 1.00 L.

6. Working standards--Pipet 15.0, 10.0, 6.0, and 2.0 mL of the nitrogen standard solution, above, into 100-mL volumetric flasks. Bring to volume with 0.1 N HCl. This will yield 150, 100, 60, and 20 mg NH_4-N/L working standards. Pipet 5 mL of the 100 mg NH_4-N/L working standard into a 100-mL volumetric flask and dilute to volume with 0.1 N HCl. This provides a 5 mg NH_4-N/L working standard. Prepare fresh working standards weekly.

7. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

8. Weighing pans, disposable.

9. Forms--Form 6A, cation exchange capacity-ammonium acetate (flow injection analysis), Form 7A, cation exchange capacity-ammonium chloride (flow injection analysis), Form QC-6A, and Form QC-7A (Appendix B, figures B-19, B-21, B-23, and B-25, respectively).

11.3.4.2 Automated Distillation-Titration--

1. Sodium chloride (NaCl).

2. Antifoam, silicone spray bottle.

3. Hydrochloric acid (HCl), 0.10 N, standardized--see Section 11.3.4.1, Step 1.

4. Boric acid (H_3BO_3), 4 percent (w/v) aqueous solution--Add 720 g boric acid to about 4 L DI water in a large stainless steel beaker. Heat to near boiling and stir until crystals dissolve. Add to a 5-gallon Pyrex bottle about 12 L DI water. Transfer hot solution through a large polyethylene funnel into the bottle. Dilute to 18 L with DI water and mix well.

5. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

6. Compressed air.

7. Weighing pans, disposable.

8. Forms--Form 6B, cation exchange capacity-ammonium acetate (titration method), Form 7B, cation exchange capacity-ammonium chloride (titration method), Form QC-6B, and Form QC-7B (Appendix B, figures B-20, B-22, B-24, and B-26, respectively).

11.3.4.3 Manual Distillation-Automatic Titration--

1. Sodium chloride (NaCl).

2. Antifoam mixture--Mix equal parts of mineral oil and octanol.

3. Boric acid (H_3BO_3), 4 percent--see Section 11.3.4.2, Step 4.

4. Hydrochloric acid (HCl), 0.1 N--see Section 11.3.4.1, Step 1.

5. Sodium hydroxide (NaOH), 1 N--Add 500 mL 50 percent NaOH solution to 8 L of DI water in a 9.5-L Pyrex solution bottle. Dilute to 9 L with DI water and mix well.

6. Zinc, granular.

7. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

8. Compressed air.

9. Beakers, plastic disposable, 250-mL.

10. Weighing pans, disposable.

11. Forms--Form 6B, cation exchange capacity-ammonium acetate (titration method), Form 7B, cation exchange capacity-ammonium chloride (titration method), Form QC-6B, and Form QC-7B (Appendix B, figures B-20, B-22, B-24, and B-26, respectively).

11.4 Calibration and Standardization

11.4.1 Flow Injection Analysis Calibration

For the FIA, use standards containing 0, 5, 20, 60, 100, and 150 mg NH_4-N/L to develop a calibration curve. A regression of the standard curve should have an intercept close to zero. Air bubbles can produce sharp sudden peaks which destroy the calibration curve. In the event of air bubbles, the calibration curve and all samples analyzed since the last quality control check sample (QCCS) must be reanalyzed. Standard values should not vary by more than 5 percent relative standard deviation (%RSD). Standardization is accomplished through use of the mechanical extractor, volumetric glassware, and repipets (automatic pipettors). Operation of repipets and calibration of balances are described in Appendix A, General Laboratory Procedures.

11.4.2 Titration Calibration

Titrants used in the automated titrations are calibrated prior to analysis to establish the normality. The normality is checked weekly. Should the check value differ from the normality by more than 5 percent, two additional checks are run and the mean of the three check values is used as the normality. The same standard titrant should be used for all samples within a batch.

11.5 Quality Control

Log all QC data on forms QC-6A, QC-6B, QC-7A, or QC-7B (Appendix B, figures B-23 through B-26, respectively); refer to Section 3.0 for additional information concerning these internal quality control checks.

Calibration Blanks--Calibration blanks should be analyzed before the initial sample analysis, at specified intervals thereafter (e.g., after every ten samples) and after the last sample of each batch. If any blank is higher than the contract required detection limit (CRDL) listed in Table 3-2, check the system and reanalyze all samples since the last acceptable calibration blank.

Reagent Blanks--Three reagent blanks, carried through the extraction procedure, are analyzed with each batch of samples for both the NH_4OAc and NH_4Cl exchange. The calculated concentration of each blank should be less than or equal to 1.05 mg N/L for FIA (0.15 meq/L) or 0.0075 meq for titrations (0.15 meq/L).

Replicates--One sample from each batch should be extracted and analyzed in duplicate. The %RSD should meet the limits in Table 3-3.

Quality Control (QC) Standards--One detection limit quality control check standard (DL-QCCS) should be analyzed for each exchange during each batch of samples. This standard should be 5.0 mg NH_4-N/L for FIA or 0.03 meq for titrations. Measured values should be within 20 percent of the known value. While permitting monitoring of instrumental detection limits, it does not replace the need to formally determine detection limits on a periodic basis (see Section 3.2.1).

QCCSs of concentrations at about mid-calibration range of the samples being analyzed should be measured before the first sample, at specified intervals thereafter (e.g., every tenth sample) and after the last sample of each batch of samples for both exchanges. Measured values for each QCCS should be within 10 percent of the known value.

Matrix Spikes--Use a solution of NH_4Cl or $(NH_4)_2SO_4$ as the spiking solution. For FIA, the final solution may be split and the matrix spike added to one of the splits. For distillation-titration, a second sample must be processed and the matrix spike must be added to the sample just prior to distillation. Recovery should be 90 to 110 percent of the spike concentration.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy windows provided by the quality assurance (QA) manager.

11.6 Procedure

Before starting the analytical procedures, valid instrumental detection limits (IDLs) are to be established, the required labware should meet the cleaning criteria described in Appendix A, General Laboratory Procedures, and the samples must have been properly prepared (see Section 4.0). Analyses should be performed as described below for NH_4OAc, then repeated for NH_4Cl. All data should be logged following the procedures given in Section 3.0.

11.6.1 Pulp Washing

NOTE: Commercial filter pulps often are contaminated and will have to be washed.

1. Prepare sample tubes by tightly compressing a 0.5-g ball of filter pulp into bottom of syringe barrel with a modified plunger. Modify the plunger by removing the rubber portion of the plunger, and cut off the plastic protrusion.

2. Add 50 mL 0.1 N HCl to the syringe containing the pulp and extract rapidly.

3. Add 50 mL DI water to the syringe containing the pulp and extract rapidly.

4. Repeat Step 3 again

5. Remove any excess solution from the washed pulp by applying gentle suction to the syringe tip. Proceed immediately with an extraction.

11.6.2 Extraction

NOTE: Figures within the square brackets, [ ], represent the form number and column in which the data are entered.

1. *For mineral soils*, weigh 5.00 g air-dry soil, place in sample tube, and record exact weight [6A-B] or [6B-B] for NH_4OAc, [7A-B] or [7B-B] for NH_4Cl. Place sample tube in upper disc of extractor and connect to inverted, tared extraction syringe, the plunger of which is inserted in the slot of the stationary disc of the extractor. Fill the syringe to the 25-mL mark with NH_4OAc. Stir sample and NH_4OAc with glass stirring rod for 15 seconds, rinse rod with NH_4OAc, and fill syringe to the 30-mL mark. Let stand for 20 minutes.

   For organic soils, weigh 1.25 g of air-dried soil into a small glass tube [6A-B] or [6B-B] for NH_4OAc, [7A-B] or [7B-B] for NH_4Cl. Add 2 mL ethanol as a wetting agent. (If the organic soil wets easily, it is not necessary to add the ethanol.) When the soil is moistened, add 15 mL NH_4OAc, cap, and shake for one hour on a reciprocating shaker. Place sample tube in upper disc of extractor and connect to inverted, tared extraction syringe, the plunger of which is inserted in the slot of the stationary disc of the extractor. Then quantitatively transfer the sample and NH_4OAc to the sample tube and fill to the 25-mL mark with NH_4OAc. Let stand for 20 minutes.

   NOTE: Up to 35-mL may be used for transfer; see Step 2.

   The exact sample weights are also recorded in column B, forms 8 through 11 for the ammonium acetate exchanges (in Section 12.0) and in column B, forms 12 through 17 for the ammonium chloride exchanges (in Section 13.0).

2. Put reservoir tube on top of sample tube; extract rapidly until NH_4OAc is at a depth of 0.5 to 1.0 cm above sample. Turn off extractor. Add about 45 mL NH_4OAc to reservoir tube, turn on extractor, and extract overnight or for approximately 16 hours. Do not allow the soil to dry between the time the extractor is turned off and back on.

   NOTE: If 35 mL are used in Step 1, reduce 45 mL to 35 mL. Total NH_4OAc or NH_4Cl used during extraction should be approximately 70 mL.

3. The next morning, switch off extractor and pull plungers down as far as extractor will allow. Disconnect syringes from sample tubes, leaving rubber connectors on sample tubes. Weigh each syringe containing the NH_4OAc extract to the nearest 0.01 g. The final weight and tare weight are used to calculate the volume of ammonium acetate extract (Section 12.0), according to the formula in Section 12.7. Final volumes are recorded in column C on forms 8 through 11 for NH_4OAc and on forms 12 through 16 for NH_4Cl.

4. Mix the extract in each syringe by shaking manually. Rinse the appropriately labeled polyethylene bottle twice with small volumes of the extract solution, then fill the bottle with extract solution and discard the excess. This solution is reserved for analysis of exchangeable cations as described in Section 12.0.

5. Return upper 2-disc unit to starting position. Attach the syringes to the sample tubes, and rinse the sides of sample tubes with ethanol from a wash bottle. Fill sample tubes to the 20-mL mark, stir, and let stand for 15 to 20 minutes. Place reservoir tube in sample tube. Extract rapidly until the level of ethanol is 0.5 to 1.0 cm above sample. Turn off

extractor and add enough ethanol to the reservoir to ensure an excess over the capacity of the syringe. Extract for 45 minutes.

6. After the extractor has stopped, turn off the switch, pull the plungers down, remove syringes, and discard the ethanol wash. Return the upper unit of the extractor to starting position, reattach syringes to the sample tube, fill reservoir tubes with about 45 mL ethanol, and extract a second time for approximately 45 minutes. When extractor has stopped, remove syringes and discard ethanol. After the second ethanol extraction, collect a few drops of ethanol extract on a spot plate. Test for residual NH_4^+ in each sample by adding four drops of Nessler's reagent to one drop of solution. If the test is positive (i.e., orange endpoint) repeat another ethanol extraction of the affected samples and test by using Nessler's reagent until a negative test is obtained. Proceed to Section 11.6.3 if using FIA, to Section 11.6.4 if using automated distillation, or to Section 11.6.5 if using manual distillation.

7. Repeat steps 1 through 6 using ammonium chloride as the exchange solution.

11.6.3 Analytical Procedure Using FIA

1. Add 50 mL of 0.1 N HCl and extract at setting of 10 (approximately one hour) and record volume [6A-C] or [7A-C].

2. Disconnect syringes and save the HCl extract for FIA analysis.

3. Operate the FIA according to manufacturer's instructions.

4. Read mg NH_4-N/L; if concentrations exceed calibration standards, dilute in the instrument calibration range and reanalyze.

5. Record data as follows:

Actual Exchange	Aliquot Volume	Diluted Volume	Instrument Reading
CEC_OAC	[6A-D]	[6A-E]	[6A-F]
CEC_CL	[7A-D]	[7A-E]	[7A-F]

11.6.4 Analytical Procedure using Automated Distillation-Titration

1. Remove sample tubes and quantitatively transfer each sample to a 250-mL digestion tube. To remove the sample, blow the filter pulp and soil out of the syringe by using a gentle flow of compressed air. Wash with a minimum of DI water. Use a rubber policeman to complete the transfer.

2. Add 6 to 7 g sodium chloride to the digestion tube, spray silicone antifoam solution into the digestion tube and connect it to the Kjeltec Auto 1030 Analyzer.

3. Follow instruction manual regarding safety and operation of the analyzer and titrate to a pH 4.60 endpoint.

4. Read mL titration and record with the normality of titrant: NH_4OAc, [6B-C], [6B-D]; NH_4Cl [7B-C], [7B-D].

11.6.5 Analytical Procedure using Manual Distillation-Automated Titration

1. Transfer sample to an 800-mL Kjeldahl flask using the procedure described in Section 11.6.4, Step 1.

2. Add 400 mL DI water, 10 g NaCl, 5 drops antifoam mixture, 1 to 2 g granular zinc, and 40 mL 1.0 N NaOH.

3. Set up Kjeldahl distillation apparatus and distill until 175-180 mL of distillate is collected in a 250-mL plastic beaker containing 50 mL of 4 percent boric acid solution.

4. Transfer plastic beaker to distillation apparatus and operate according to manufacturer's instructions.

5. Read mL titration and record with the normality of titrant as described in Section 11.6.4, NH_4OAc: [6B-C], [6B-D]; NH_4Cl: [7B-C], [7B-D].

11.7 Calculations

NOTE: Designations within the square brackets, [ ], represent the Form number and column in which the data are entered on forms 6A, 7A, 6B, and 7B (Appendix B, figures B-19, B-21, B-20, and B-22).

11.7.1 Flow Injection Analysis

CEC (meq/100 g) = {(([Final Sol. Vol.] × [Inst. Reading]) × ([Total Diluted Vol.] + [Aliquot Vol.]) × 1 L} + {[1,000 mL × 1 meq + 14 mg × 1] + (sample wt. × (1-[MOIST]) + (100 + [MOIST])}

CEC_OAC [6A-G] = {(([6A-C] × [6A-F]) × ([6A-E] ÷ [6A-D]) × 1} + {[6A-B] × (1 - [1-D]) + (100 + [1-D])}

CEC_CL [7A-G] = {(([7A-C] × [7A-F]) × ([7A-E] + [7A-D]) × 1} + {[7A-B] × (1 - [1-D]) + (100 + [1-D])}

11.7.2 Titration

[CEC (meq/100 g)] = {[Titrant Volume] × [Normality] × 1} + {[sample wt.] × (1 - [MOIST]) + (100 + [MOIST]) × 100}

CEC_OAC [6B-E] = {[6B-C] × [6B-D] × 1} + {[6B-B] × (1 - [1-D]) + (100 + [1-D]) × 100}

CEC_CL [7B-E] = {[7B-C] × [7B-D] × 1} + {[7B-B] × (1 - [1-D]) + (100 + [1-D]) × 100}

11.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water,* D-1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Doxsee, K. 1985. *Cation Exchange Capacity in Nursery Soils Using FIA (Flow Injection Analysis).* Am. No. 1503-15. Weyerhaeuser Technology Center, Research Division, Tacoma, Washington.

Rhoades, J. D. 1982. Cation Exchange Capacity, pp. 149-158. In: *Methods of Soil Analysis: Part 2-Chemical and Microbiological Properties,* Second Edition, A. L. Page, R. H. Miller, and D. R. Keeney (eds.). American Society of Agronomy, Inc./Soil Science Society of America, Inc., Madison, Wisconsin.

U.S. Department of Agriculture/Soil Conservation Service. 1972. *Procedures for Collecting Soil Samples and Methods of Analysis for Soil Surveys.* Soil Survey Investigations Report No. 1, U.S. Department of Agriculture. U.S. Government Printing Office, Washington, D.C.

U.S. Department of Agriculture/Soil Conservation Service. 1984. *Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples.* Soil Survey Investigations Report No. 1, U.S. Department of Agriculture. U.S. Government Printing Office, Washington, D.C.

12.0 Exchangeable Cations in Ammonium Acetate

12.1 Overview

The exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) in the soil can be used to estimate the ability of a soil to buffer acidic deposition. Ammonium chloride and buffered ammonium acetate are used to extract exchangeable base cations at pH values near the soil pH and at the buffered pH of 7.0, respectively.

Base saturation is defined as the sum of exchangeable base cations divided by the cation exchange capacity (CEC) and is expressed as a percentage. Cation exchange sites not occupied by base cations are assumed to be occupied by acidic cations such as hydrogen and aluminum.

CEC is a measure of the buffering capacity of the soil. Base saturation relates to how much buffering capacity remains in the soil. Exchangeable acidity is a measure of the amount of exchangeable acidic cations on the soil cation exchange complex.

12.1.1 Summary of Method

Previously prepared extracts from the CEC procedure (Section 11.0) are analyzed for calcium, magnesium, potassium, and sodium. Once the concentration of each cation in the soil extract is determined, the cation concentrations in the original soil sample may be calculated.

Atomic absorption spectroscopy (AA) can be used to measure calcium, magnesium, potassium, and sodium. A light beam from a hollow cathode lamp, whose cathode is made of the element to be determined, is directed through the flame into a monochromator and onto a detector that measures the amount of light passing through the flame. Absorption depends upon the presence of free, unexcited, ground state atoms in the flame. Since the wavelength of the light beam is characteristic only of the cation being determined, the light energy absorbed by the flame is a measure of the concentration of that cation in the extract. A complete discussion of AA methods is provided in Appendix C.

Inductively coupled plasma spectroscopy (ICP) can be used to measure calcium, magnesium, and sodium. Samples are nebulized to produce an aerosol. The aerosol is transported by an argon carrier stream to an inductively coupled argon plasma, which is produced by a radio frequency generator. In the plasma (which is at a temperature of 6,000 to 10,000 °K) the analytes in the aerosol are atomized, ionized, and ionic emission spectra is produced. The spectra from all analytes are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed by a computer system. The signal is proportional to the analyte concentration and is calibrated by analyzing a series of standards (U.S. Environmental Protection Agency [USEPA], 1983; Fassel, 1982). A thorough discussion of ICP methods is provided in Appendix D.

Emission spectroscopy (ES) can be used to measure potassium and sodium. The sample is aspirated into a gas flame and excitation is carried out under carefully controlled and reproducible conditions. The desired spectral line is isolated by the use of interference filters or by a suitable slit arrangement in light-dispersing devices such as prisms or gratings. The intensity of light is measured by a phototube potentiometer or other appropriate circuit. The intensity of light at the appropriate wavelength (e.g., 589 nm for Na^+) is approximately proportional to the concentration of the element. A discussion of ES methods is provided in Appendix E.

12.1.2 Interferences

Three types of interferences, spectral, chemical, and physical, can be identified for the analytical portion of the method. These vary in importance depending on the particular analytical procedure chosen. Additional details of these interferences and means for their obviation, elimination, or compensation are provided in appendices C, D, and E.

Spectral interferences are generally caused by spectral overlap from another element or background contributions. These interferences can usually be corrected by monitoring and compensating for the effect of interfering elements, selecting another wavelength, correcting background effects, or using a narrower slit width.

Chemical interferences are often caused by the cations forming molecular compounds instead of dissociated ions. This interference, most pronounced with the multivalent ions (such as Ca^{2+} and Mg^{2+}), is negligible with the ICP technique. This interference is often corrected by the addition of lanthanum or lithium or by the avoidance of anions such as sulfate and phosphate.

The most common physical interference in the analysis of soils exchange solutions is salt build-up clogging the burner or nebulizer. Although dilution will reduce this problem, it will also change the matrix and any effect it may have on the instrument read-out.

Matrix effects are usually compensated by analyzing samples and all calibration standards, reagent blanks, and quality control (QC) standards in the same matrix. Matrix effects may be tested by serial dilutions, spiked additions, and comparison with an alternative method of analysis. When the matrix effects are significant and cannot be readily corrected, the analyses must be performed by standard additions (see appendices C and D).

12.1.3 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids and hydroxide solutions should be restricted to a fume hood. Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

Follow the safety precautions of the manufacturer when operating instruments. Gas cylinders should always be chained or bolted in an upright position.

12.2 Sample Collection, Preservation, and Storage

This procedure uses the soil saturation aliquots prepared as described in Section 11 (see specifically, sections 11.2 and 11.6.2).

12.3 Equipment and Supplies

12.3.1 Equipment Specifications

12.3.1.1 Determination by Atomic Absorption--

1. Spectrophotometer, with grating monochromator, photomultiplier detector, adjustable slits, and a wavelength range of 190 to 800 nm.

2. Burner, as recommended by the instrument manufacturer. When nitrous oxide is used as the oxidant, a nitrous oxide burner is required.
3. Hollow cathode lamps, single element lamps preferred; multielement lamps may be used. Electrodeless discharge lamps may be used where available.
4. Balance, capable of weighing to 0.1 g.
5. Balance calibration weights, 3-5 weights covering expected range.

12.3.1.2 Determination by Inductively Coupled Plasma--

1. Inductively Coupled Plasma-Atomic Emission Spectrometer.
2. Balance, capable of weighing to 0.001 g.
3. Balance calibration weights, 3-5 weights covering expected range.

12.3.1.3 Determination by Emission Spectroscopy--

1. Emission spectrometer, direct-reading or internal-standard type; or an atomic absorption spectrometer operated in the flame emission mode.
2. Balance, capable of weighing to 0.001 g.
3. Balance calibration weights, 3-5 weights covering expected range.

12.3.2 Reagents and Consumable Materials

Acids used in the preparation of standards and for sample processing must be ultra-high purity grade (e.g., Baker Ultrex grade or SeaStart Ultrapure grade). To minimize concentration of cations in standard solutions by evaporation, store solutions in linear or high density polyethylene bottles. Use small containers to reduce the amount of dry element that may be picked up from the bottle walls when the solution is poured.

Deionized (DI) water used for preparing or diluting reagents, standards, and samples must meet purity specifications for Type I reagent water as given in ASTM D 1193 (ASTM, 1984).

12.3.2.1 Determination by Atomic Absorption--

1. Hydrochloric acid, concentrated (12 M HCl)--Ultrapure grade, Baker Instra-Analyzed or equivalent.
2. HCl (1 percent v/v)--Add 5 mL concentrated HCl to 495 mL deionized (DI) water.
3. Nitric acid, concentrated--Ultrapure grade, Baker Instra-Analyzed or equivalent.
4. Nitric acid (0.5 percent v/v HNO_3)--Add 0.50 mL HNO_3 to 50 mL DI water and dilute to 100 mL.

5. Primary standard solutions--Prepare from ultra-high purity grade chemicals as directed in the individual procedures. Commercially available stock standard solutions may also be used.

6. Dilute calibration standards--Prepare a series of standards of the cation by dilution of the appropriate stock metal solution in the specific matrix to cover the concentration range desired. Prepare all calibration standards in concentration units of mg/L.

7. Fuel--Commercial grade acetylene with in-line filter is generally acceptable.

8. Oxidant--Air may be supplied from a compressed-air line, a laboratory compressor, or from a cylinder of compressed air. Nitrous oxide is supplied from a cylinder of compressed gas.

9. Lanthanum chloride ($LaCl_3$) matrix modifier solution--Dissolve 29 g La_2O_3, slowly and in small portions, in 250 mL concentrated HCl.

   Caution: Reaction is violent. Dilute to 500 mL with DI water.

10. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

11. Weighing pans, disposable.

12. Forms--Form 8 calcium in ammonium acetate, Form 9 magnesium in ammonium acetate, Form 10 potassium in ammonium acetate, Form 11 sodium in ammonium acetate, Form QC-8, Form QC-9, Form QC-10, and Form QC-11 (Appendix B, figures B-27 through B-34, respectively).

12.3.2.2 Determination by Inductively Coupled Plasma--

1. Hydrochloric acid, concentrated (12 M HCl, specific gravity 1.19)--Ultrapure grade, Baker Instra-Analyzed or equivalent.

2. Hydrochloric acid (50 percent v/v)--Add 500 mL concentrated HCl to 400 mL DI water and dilute to 1.00 L with DI water.

3. Nitric acid, concentrated (specific gravity 1.41)--Ultrapure grade, Baker Instra-Analyzed or equivalent.

4. Nitric acid (50 percent v/v)--Add 500 mL concentrated HNO_3 to 400 mL DI water and dilute to 1 L.

5. Primary standard solutions--May be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for one hour at 105 °C unless otherwise specified.

6. Argon, oxygen-free.

7. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

8. Weighing pans, disposable.

9. Forms--Form 8 calcium in ammonium acetate, Form 9 magnesium in ammonium acetate, Form 11 sodium in ammonium acetate, Form QC-8, Form QC-9, and Form QC-11 (Appendix B, figures B-27, B-28, B-30, B-31, B-32, and B-34, respectively).

12.3.2.3 Determination by Emission Spectroscopy--

1. Standard lithium solution--Use either lithium chloride (LiCl) or lithium nitrate ($LiNO_3$) to prepare standard lithium solution containing 1,000 mg Li/L.

   Dry LiCl overnight in an oven at 105 °C. Rapidly weigh 6.109 g LiCl and dissolve in 1.0 N NH_4OAc, as needed to match the sample extract matrix. Dilute to 1,000 mL with the same 1.0 N NH_4OAc solution.

   Dry $LiNO_3$ overnight in an oven at 105 °C. Rapidly weigh 9.935 g $LiNO_3$ and dissolve in 1.0 N NH_4OAc, as needed to match the sample extract matrix. Dilute to 1,000 mL with the same 1.0 N NH_4OAc solution.

   Prepare a new calibration curve whenever the standard lithium solution is changed. Do not change solutions within a batch.

   NOTE: Lithium is used to suppress ionization of K^+ and Na^+.

2. Primary standard solutions--May be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for one hour at 105 °C unless otherwise specified.

3. Acetylene (commercial grade or better).

4. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

5. Weighing pans, disposable.

6. Forms--Form 10 potassium in ammonium acetate, Form 11 sodium in ammonium acetate, Form QC-10, and Form QC-11 (Appendix B, figures B-29, B-30, B-33, and B-34, respectively).

12.4 Calibration and Standardization

Within each class of instruments (AA, ICP, and ES), the calibration procedure varies slightly. Calibrate by analyzing a calibration blank and a series of at least three standards within the linear range. If an ICP is used, a multielement standard may be prepared and analyzed. For AA and ES determinations, the instrument must be calibrated for each analyte by using a separate stan-dard. The concentration of standards should bracket the expected sample concentration; however, the linear range of the instrument should not be exceeded. Details of calibration are discussed in appendices C, D, and E for AA, ICP, and ES, respectively.

12.5 Quality Control

Log all quality control (QC) data on forms QC-8, QC-9, QC-10, and QC-11 (Appendix B, figures B-31 through B-34); refer to Section 3.0 for additional information regarding these internal quality control checks.

Calibration Blanks--Calibration blanks for each cation should be analyzed before the initial sample analysis, at specified intervals thereafter (e.g., after every ten samples) and after the last sample of each batch. If any blank is higher than the contract-required detection limit (CRDL) listed in Table 3-2, check the system and reanalyze all samples since the last acceptable calibration blank.

Reagent Blanks--Three reagent blanks, carried through the extraction procedure, are analyzed with each batch of samples for each cation. The concentration of each blank should be less than or equal to the CRDL outlined in Table 3-2.

Replicates--One sample from each batch should be extracted and analyzed in duplicate. The percent relative standard deviation (%RSD) should meet the limits in Table 3-3.

QC Standards--One detection limit quality control check standard (DL-QCCS) should be analyzed for each cation with each batch of samples. The known concentrations in the DL-QCCS samples should be about 0.20 mg of each of the cations per liter of 1.0 N NH_4OAc. Measured values should be within 20 percent of known values of the DL-QCCS standards.

QCCSs of concentrations at about mid-calibration range of the samples being analyzed should be measured for each cation before the first sample, at specified intervals thereafter, e.g. (every tenth sample) and after the last sample of each batch of samples for both exchanges. Measured values for each QCCS should be within 10 percent of the known value.

Matrix Spike--For each batch of soils, a matrix spike is made to the exchange solution for each parameter analyzed in the sample. The known spike value should be 1.5 to 3.0 times the measured concentration, or ten times the CRDL, whichever is greater. Calculated recovery of the spike should be 90 to 110 percent of the known concentration of the spike.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy windows provided by the quality assurance (QA) manager.

12.6 Procedure

Before proceeding with the analytical procedure, the analyst should be certain that all QC procedures have been implemented, all labware has been properly cleaned, and valid instrumental detection limits (IDLs) have been obtained, as outlined in Section 3.0 and Appendix A.

General procedures for AA, ICP, and ES are given in sections 12.6.1, 12.6.2, and 12.6.3, respectively. Detailed procedures are provided in appendices C, D, and E.

NOTE: Figures within the square brackets, [ ], represent the form number and column in which the data are entered.

12.6.1 Procedure for Determinations by Atomic Absorption

Differences among AA spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the operating instructions for the particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, allow the lamp to warm up for a minimum of 15 minutes unless the instrument is operated in a double-beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the recommendation of the manufacturer. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the analyte and calibrate the instrument. Aspirate the samples and determine the concentrations either directly (if the instrument reads directly in concentration units) or from a calibration curve.

12.6.1.1 Calcium and Magnesium--

1. To each 10.0-mL volume of calibration standard, blank, and sample (soil extract), add 1.00 mL $LaCl_3$ solution. Dilute with DI water to 20 mL.

2. Calibrate the instrument.

3. Analyze the samples.

   NOTE: Initial readout should be made on the 1:1 soil extract:DI water dilution *before* any additional dilutions are made. For further dilutions, use a 1:1 water:extraction solution (i.e., 50 percent extracting solution) as the dilution agent.

4. Dilute and reanalyze any samples for which the concentration exceeds the linear range, as outlined in Step 1. Record aliquot and diluted volumes: Ca^{2+}, [8-D], [8-E]; Mg^{2+} [9-D], [9-E].

5. Record results as mg/L in the diluted solution: Ca^{2+} [8-F]; Mg^{2+} [9-F].

12.6.1.2 Potassium and Sodium--

1. Calibrate the instrument.

2. Analyze the samples.

NOTE: Initial readout should be made on the 1:1 soil extract:DI water dilution *before* any additional dilutions are made. For further dilutions, use a 1:1 water:extraction solution (i.e., 50 percent extracting solution) as the dilution agent.

3. Dilute and reanalyze any sample for which the concentration exceeds the calibrated range and record aliquot and diluted volumes for K^+ [10-D], [10-E]; for Na^+ [11-D], [11-E].

   NOTE: Record "1.0" in columns D and E for all samples in which no dilutions were required.

4. Record results as mg/L in the soil extract; if the aliquot was diluted, record the diluted volume: K^+, [10-F]; Na^+, [11-F].

12.6.2 *Procedure for Determinations by Inductively Coupled Plasma*

1. Set up the instrument as recommended by the manufacturer. The instrument must be allowed to become thermally stable before analysis begins (10 to 30 minutes).
2. Profile and calibrate the instrument according to the recommended procedures of the manufacturer. Flush the system with the calibration blank between each standard.
3. Begin sample analysis, flushing the system with the calibration blank solution between each sample.
4. Dilute with 1:1 extract:DI water solution and reanalyze any samples for which the concentration exceeds the calibration range, and report aliquot and diluted volumes; Ca^{2+} [8-D], [8-E]; Mg^{2+} [9-D], [9-E]; Na^+ [11-D], [11-E].
5. Record results for Ca^{2+} [8-F], Mg^{2+} [9-F], and Na^+ [11-F] and analyze K^+ by AA or ES.

12.6.3 *Procedure for Determinations by Emission Spectroscopy*

NOTE: Locate instrument in an area away from direct sunlight or in an area free of drafts, dust, and tobacco smoke. Guard against contamination from corks, filter paper or pulp, perspiration, soap, cleansers, cleaning mixtures, and inadequately rinsed apparatus. Follow recommendation of the manufacturer for selecting proper photocell and wavelength, for adjusting slit width and sensitivity, for appropriate fuel and oxidant pressures, and for the steps required for warm-up, correcting for interferences and flame background, rinsing of burner, igniting sample, and measuring emission intensity.

1. Calibrate the instrument.
2. Analyze the samples.
3. Dilute with 1:1 soil extract:DI water solution and reanalyze any samples for which the concentration exceeds the calibration range and report aliquot and diluted volumes: K^+, [10-D] and [10-E]; Na^+, [11-D] and [11-E].
4. Record results for K^+ [10-F] and Na^+ [11-F] and analyze Ca^{2+} and Mg^{2+} by AA or ICP.

12.7 Calculations

NOTE: Designations within the square brackets, [ ], represent the form number and column in which the data are entered on forms 8, 9, 10, 11, and 1 (Appendix B, figures B-27, B-28, B-29, B-30, and B-9).

Recovered Extract Volume = (Final Weight – Tare Weight) ÷ Density (weight data from Section 11.6.2, Step 3).

Final Extract Vol. [8-C], [9-C], [10-C], or [11-C] = (Final Wt. (g) – Tare Wt. (g)) ÷ 1.0124

Exch. Cation (meq/100 g) = {[inst. reading] × ([total diluted vol.] ÷ [aliq. vol.]) × [final extract vol.] × 1 L ÷ 1000 mL × 100 × meq ÷ at. wt. (mg) × 1} ÷ {[sample wt.] × (1 - [MOIST]) ÷ (100 + [MOIST]))}

CA_OAC [8-G] = {[8-F] × ([8-E] ÷ [8-D]) × [8-C] × 0.1 × 0.0499 × 1} ÷ {[8-B] × (1 - [1-D]) ÷ (100 + [1-D]))}

MG_OAC [9-G] = {[9-F] × ([9-E] ÷ [9-D]) × [9-C] × 0.1 × 0.0822 × 1} ÷ {[9-B] × (1 - [1-D]) ÷ (100 + [1-D]))}

K_OAC [10-G] = {[10-F] × ([10-E] ÷ [10-D]) × [10-C] × 0.1 × 0.0255 × 1} ÷ {[10-B] × (1 - [1-D]) ÷ (100 + [1-D]))}

NA_OAC [11-G] = {[11-F] × ([11-E] ÷ [11-D]) × [11-C] × 0.1 × 0.0435 × 1} ÷ {[11-B] × (1 - [1-D]) ÷ (100 + [1-D]))}

12.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water*, D1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Fassel, V. A. 1982. Analytical Spectroscopy with Inductively Coupled Plasmas - Present Status and Future Prospects. In: *Recent Advances in Analytical Spectroscopy*. Pergamon Press, New York, New York.

U.S. Environmental Protection Agency. 1983 (revised). *Methods for Chemical Analysis of Water and Wastes, Method 200.0, Atomic Absorption Methods; and Method 200.7, Inductively Coupled Plasma-Atomic Emission Spectrometric Method for the Trace Element Analysis of Water and Wastes*. EPA 600/4-79/020. U.S. Environmental Protection Agency, Cincinnati, Ohio.

13.0 Exchangeable Cations in Ammonium Chloride

13.1 Overview

The exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, and Al^{3+}) obtained in unbuffered 1.0 N NH_4Cl represent the effective exchange that occurs at field pH. Values of the exchangeable cations determined by this procedure are theoretically equal to those determined by the buffered NH_4OAc exchange (Section 12.0). The concentrations (meq/100 g) of the exchangeable cations plus acidity should approximate the cation exchange capacity (CEC) (Section 11.0).

Base saturation is given as the total amount of exchangeable base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) divided by the CEC. Exchangeable acidity is a measure of the amount of exchangeable acidic cations on the soil cation exchange complex.

13.1.1 Summary of Method

Previously prepared extracts from the CEC procedure (Section 11.0) are analyzed for aluminum, calcium, magnesium, potassium, and sodium. Once the concentration of each cation in the soil extract is determined, the cation concentrations in the original soil sample may be calculated.

Atomic absorption spectroscopy (AA) can be used to measure calcium, magnesium, potassium, and sodium. A light beam from a hollow cathode lamp, whose cathode is made of the element to be determined, is directed through the flame into a monochromator and onto a detector that measures the amount of light passing through the flame. Absorption depends upon the presence of free, unexcited, ground state atoms in the flame. Since the wavelength of the light beam is characteristic only of the cation being determined, the light energy absorbed by the flame is a measure of the concentration of that cation in the extract. A complete discussion of AA methods is provided in Appendix C.

Inductively coupled plasma spectroscopy (ICP) must be used to measure aluminum and can be used to measure calcium, magnesium, and sodium. Samples are nebulized to produce an aerosol. The aerosol is transported by an argon carrier stream to an inductively coupled argon plasma, which is produced by a radio frequency generator. In the plasma (which is at a temperature of 6,000 to 10,000 °K) the analytes in the aerosol are atomized, ionized, and ionic emission spectra is produced. The spectra from all analytes are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed by a computer system. The signal is proportional to the analyte concentration and is calibrated by analyzing a series of standards (U.S. EPA, 1983; Fassel, 1982). A thorough discussion of ICP methods is provided in Appendix D.

Emission spectroscopy (ES) can be used to measure potassium and sodium. The sample is aspirated into a gas flame and excitation is carried out under carefully controlled and reproducible conditions. The desired spectral line is isolated by the use of interference filters or by a suitable slit arrangement in light-dispersing devices such as prisms or gratings. The intensity of light is measured by a phototube potentiometer or other appropriate circuit. The intensity of light at the appropriate wavelength (e.g., 589 nm for Na^+) is approximately proportional to the concentration of the element. A discussion of ES methods is provided in Appendix E.

13.1.2 Interferences

No interferences are known for the extraction and acid titration, but several interferences may occur during analysis of the exchangeable cations, including spectral, chemical, physical, and matrix effects. Additional details of these interferences and means for their obviation, elimination, or compensation are provided in appendices C, D, and E.

Spectral interferences are generally caused by spectral overlap from another element or background contributions. These interferences can usually be corrected by monitoring and compensating for the effect of interfering elements, selecting another wavelength, correcting background effects, or using a narrower slit width.

Chemical interferences are often caused by the cations forming molecular compounds instead of dissociated ions. This interference, most pronounced with the multivalent ions (such as Ca^{2+}, Mg^{2+}, and especially Al^{3+}), is negligible with the ICP technique. This interference is often corrected by the addition of lanthanum or lithium or by the avoidance of anions such as sulfate and phosphate.

The most common physical interference in the analysis of soils exchange solutions is salt build-up clogging the burner or nebulizer. Although dilution will reduce this problem, it will also change the matrix and any effect it may have on the instrument read-out.

Matrix effects are usually compensated for by analyzing samples and all calibration standards, reagent blanks, and quality control (QC) standards in the same matrix. Matrix effects may be tested by serial dilutions, spiked additions, and comparison with an alternative method of analysis. When the matrix effects are significant and cannot be readily corrected, the analyses must be performed by standard additions (see appendices C and D)..

13.1.3 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids and hydroxide solutions should be restricted to a fume hood. Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

Follow the safety precautions of the manufacturer when operating instruments. Gas cylinders should always be chained or bolted in an upright position.

13.2 Sample Collection, Preservation, and Storage

This procedure uses the soil saturation aliquots prepared as described in Section 11 (see specifically, sections 11.2 and 11.6.2).

13.3 Equipment and Supplies

13.3.1 Equipment Specifications

13.3.1.1 Determination by Atomic Absorption--

1. Spectrophotometer, with grating monochromator, photomultiplier detector, adjustable slits, and a wavelength range of 190 to 800 nm.

2. Burner, as recommended by the instrument manufacturer. When nitrous oxide is used as the oxidant, a nitrous oxide burner is required.

3. Hollow cathode lamps, single element lamps preferred; multielement lamps may be used. Electrodeless discharge lamps may be used where available.

4. Balance, capable of weighing to 0.1 g.

5. Balance calibration weights, 3-5 weights covering expected range.

13.3.1.2 Determination by Inductively Coupled Plasma--

1. Inductively Coupled Plasma-Atomic Emission Spectrometer.

2. Balance, capable of weight to 0.01 g.

3. Balance calibration weights, 3-5 weights covering expected range.

13.3.1.3 Determination by Emission Spectroscopy--

1. Flame photometer, direct-reading or internal-standard type; or an atomic absorption spectrometer operated in the flame emission mode.

2. Balance, capable of weighing to 0.001 g.

3. Balance calibration weights, 3-5 weights covering expected range.

13.3.2 Reagents and Consumable Materials

Acids used in the preparation of standards and for sample processing must be of ultra-high purity grade (e.g., Baker Ultrex grade or SeaStart Ultrapure grade). To minimize concentration of cations in standard solutions by evaporation, store solutions in linear or high density polyethylene bottles. Use small containers to reduce the amount of dry element that may be picked up from the bottle walls when the solution is poured. Shake each container thoroughly before use to redissolve any accumulated salts from the walls.

Deionized (DI) water used for preparing or diluting reagents, standards, and samples must meet purity specifications for Type I reagent water as given in ASTM D 1193 (ASTM, 1984).

13.3.2.1 Determination by Atomic Absorption--

1. Hydrochloric acid, concentrated (12 M HCl)--Ultrapure grade, Baker Instra-Analyzed or equivalent.

2. HCl (1 percent v/v)--Add 5 mL concentrated HCl to 495 mL DI water.

3. Nitric acid, concentrated--Ultrapure grade, Baker Instra-Analyzed or equivalent.

4. Nitric acid (0.5 percent v/v HNO_3)--Add 0.50 mL HNO_3 to 50 mL DI water and dilute to 100 mL.

5. Primary standard solutions--Prepare from ultra-high purity grade chemicals as directed in the individual procedures. Commercially available stock standard solutions may also be used.

6. Dilute calibration standards--Prepare a series of standards of the cation by dilution of the appropriate stock metal solution in the specific matrix to cover the concentration range desired. Prepare all calibration standards in concentration units of mg/L.

7. Fuel--Commercial grade acetylene with in-line filter is generally acceptable.

8. Oxidant--Air may be supplied from a compressed-air line, a laboratory compressor, or from a cylinder of compressed air. Nitrous oxide is supplied from a cylinder of compressed gas.

9. Lanthanum chloride ($LaCl_3$) matrix modifier solution--Dissolve 29 g La_2O_3, slowly and in small portions, in 250 mL of concentrated HCl.

   Caution: Reaction is violent. Dilute to 500 mL with DI water.

10. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

11. Weighing pans, disposable.

12. Forms--Form 12, calcium in ammonium chloride, Form 13, magnesium in ammonium chloride, Form 14, potassium in ammonium chloride, Form 15, sodium in ammonium chloride, Form QC-12, Form QC-13, Form QC-14, and Form QC-15 (Appendix B, figures B-35 through B-38 and B-40 through B-43, respectively).

13.3.2.2 Determination by Inductively Coupled Plasma--

1. Hydrochloric acid, concentrated (12 M HCl, specific gravity 1.19)--Ultrapure grade, Baker Instra-Analyzed or equivalent.

2. Hydrochloric acid (50 percent v/v)--Add 500 mL concentrated HCl to 400 mL DI water and dilute to 1.00 L with DI water.

3. Nitric acid, concentrated (specific gravity 1.41)--Ultrapure grade, Baker Instra-Analyzed or equivalent.

4. Nitric acid (50 percent v/v)--Add 500 mL concentrated HNO_3 to 400 mL DI water and dilute to 1 L.

5. Primary standard solutions--May be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for one hour at 105 °C unless otherwise specified.

6. Argon, oxygen-free.

7. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

8. Weighing pans, disposable.

9. Forms--Form 12, calcium in ammonium chloride, Form 13, magnesium in ammonium chloride, Form 15, sodium in ammonium chloride, Form 16, aluminum in ammonium chloride, Form QC-12, Form QC-13, Form QC-15, and Form QC-16 (Appendix B, figures B-35, B-36, B-38 through B-41, B-43, and B-44, respectively).

13.3.2.3 Determination by Emission Spectroscopy--

1. Standard lithium solution--Use either lithium chloride (LiCl) or lithium nitrate ($LiNO_3$) to prepare standard lithium solution containing 1,000 mg Li/L.

   NOTE: Lithium is used to suppress ionization of K^+ and Na^+.

   Dry LiCl overnight in an oven at 105 °C. Rapidly weigh 6.109 g LiCl and dissolve in 1.0 N NH_4OAc, as needed to match the sample extract matrix. Dilute to 1,000 mL with the same 1.0 N NH_4OAc solution.

   Dry $LiNO_3$ overnight in an oven at 105 °C. Rapidly weigh 9.935 g $LiNO_3$ and dissolve in 1.0 N NH_4OAc, as needed to match the sample extract matrix. Dilute to 1,000 mL with the same 1.0 N NH_4OAc solution.

   Prepare a new calibration curve whenever the standard lithium solution is changed. Do not change solutions within a batch.

2. Primary standard solutions--May be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for one hour at 105 °C unless otherwise specified.

3. Acetylene (commercial grade or better).

4. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

5. Weighing pans, disposable.

6. Forms--Form 14, potassium in ammonium chloride, Form 15, sodium in ammonium chloride, Form QC-14, and Form QC-15 (Appendix B, figures B-37, B-38, B-42, and B-43, respectively).

13.4 Calibration and Standardization

Within each class of instruments (AA, ICP, and ES), the calibration procedure varies slightly. Calibrate by analyzing a calibration blank and a series of at least three standards within the linear range. If an ICP is used, a multielement standard may be prepared and analyzed. For AA and ES determinations, the instrument must be calibrated for each analyte by using a separate stan-dard. The concentration of standards should bracket the expected sample concentration; however, the linear range of the instrument should not be exceeded. Details of calibration are discussed in appendices C, D, and E for AA, ICP, and ES, respectively.

13.5 Quality Control

Log all quality control (QC) data on forms QC-12, QC-13, QC-14, QC-15, and QC-16 (Appendix B, figures B-40 through B-44); refer to Section 3 for additional information regarding these internal quality control checks.

Calibration Blanks--Calibration blanks for each cation should be analyzed before the initial sample analysis, at specified intervals thereafter (e.g., after every ten samples) and after the last sample of each batch. The calculated concentrations for each blank should be less than 0.10 mg/L for Al^{3+} and less than 0.05 mg/L for the other exchangeable cations. If any blank is higher than these limits, check the system and reanalyze all samples since the last acceptable calibration blank.

Reagent Blanks--Three reagent blanks, carried through the extraction procedure, are analyzed with each batch of samples for each cation. The concentration of each blank should be less than or equal to the contract-required detection limit (CRDL) listed in Table 3-2.

Replicates--One sample from each batch should be extracted and analyzed in duplicate. The percent relative standard deviation (%RSD) should meet the limits outlined in Table 3-3.

QC Standards--One detection limit quality control check standard (DL-QCCS) should be analyzed for each cation with each batch of samples. The concentration of this DL-QCCS should be about 0.30 mg/L for Al^{3+} and 0.15 mg/L for other exchangeable cations. Measured values should be within 20 percent of the known value of the DL-QCCS standards.

QCCSs of concentrations at about mid-calibration range of the samples being analyzed should be measured for each cation before the first sample, at specified intervals thereafter (e.g., every tenth sample) and after the last sample of each batch of samples for both exchanges. Measured values for each QCCS should be within 10 percent of the known value.

Matrix Spike--For each batch of soils, a matrix spike is made to the exchange solution for each parameter analyzed in the sample. The known spike value should be 1.5 to 3.0 times the measured concentration, or ten times the CRDL, whichever is greater. Calculated recovery of the spike should be 90 to 110 percent of the known concentration of the spike.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy windows provided by the quality assurance (QA) manager.

13.6 Procedure

Before proceeding with the analytical procedure, the analyst should be certain that all QC procedures have been implemented, all labware has been cleaned properly, and valid instrumental detection limits (IDLs) have been obtained as outlined in Section 3.0 and Appendix A.

General procedures for AA, ICP, and ES are given in sections 13.6.1, 13.6.2, and 13.6.3, respectively. Detailed procedures are provided in appendices C, D, and E.

NOTE: Figures within the square brackets, [ ], represent the form number and column in which the data are entered.

13.6.1 Procedure for Determinations by Atomic Absorption

NOTE: AA can be used to determine all exchangeable cations with the exception of aluminum, which must be done on ICP.

Differences among AA spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the operating instructions for his particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, allow the lamp to warm up for a minimum of 15 minutes unless the instrument is operated in a double-beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the recommendation of the manufacturer. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the analyte and calibrate the instrument. Aspirate the samples and determine the concentrations either directly (if the instrument reads directly in concentration units) or from a calibration curve.

13.6.1.1 Calcium and Magnesium--

1. Add 1.0 mL of $LaCl_3$ solution to a 10-mL volume of each calibration standard, blank, and sample. Dilute with DI water to 20 mL. Record the final extract solution volume: Ca^{2+} [12-C]; Mg^{2+} [13-C].

2. Calibrate the instrument.

3. Analyze the samples.

   NOTE: Initial readout should be made on the 1:1 soil extract:DI water dilution *before* any additional dilutions are made. For further dilutions, use a 1:1 DI water:extraction solution (i.e., 50 percent extracting solution) as the dilution agent.

4. Dilute and reanalyze any samples for which the concentration exceeds the linear range, as outlined in Step 1. Record aliquot and diluted volumes: Ca^{2+}, [12-D], [12-E]; Mg^{2+}, [13-D], [13-E].

5. Record results as mg/L in the soil extract: Ca^{2+} [12-F]; Mg^{2+} [13-F].

13.6.1.2 Potassium and Sodium--

1. Calibrate the instrument.

2. Analyze the samples.

   NOTE: Initial readout should be made on the 1:1 soil extract:DI water dilution *before* any additional dilutions are made. For further dilutions, use a 1:1 DI water:extraction solution (i.e., 50 percent extracting solution) as the dilution agent.

3. Dilute and reanalyze any sample for which the concentration exceeds the calibrated range, and record aliquot and diluted volumes; K^+ [14-D]; [14-E]; Na^+, [15-D], [15-E].

4. Record results as mg/L in the soil extract: K^+ [14-F]; Na^+ [15-F].

13.6.2 Procedure for Determinations by Inductively Coupled Plasma

1. Set up the instrument as recommended by the manufacturer. The instrument must be allowed to become thermally stable before analysis begins (10 to 30 minutes).

2. Profile and calibrate the instrument according to the recommended procedures of the manufacturer. Flush the system with the calibration blank between each standard.

3. Begin sample analysis, flushing the system with the calibration blank solution between each sample.

4. Dilute with 1:1 extract:DI water solution and reanalyze any samples for which the concentration exceeds the calibration range, and report aliquot and diluted volumes; Ca^{2+} [12-D], [12-E]; Mg^{2+} [13-D], [13-E]; Na^+, [15-D], [15-E]; Al^{3+}, [16-D], [16-E].

5. Record results for Ca^{2+}, [12-F]; Mg^{2+} [13-F]; Na^+ [15-F]; and Al^{3+} [16-F]. Analyze K^+ by AA or ES.

13.6.3 Procedure for Determinations by Emission Spectroscopy

NOTE: Locate instrument in an area away from direct sunlight and in an area free of drafts, dust, and tobacco smoke. Guard against contamination from corks, filter paper or pulp, perspiration, soap, cleansers, cleaning mixtures, and inadequately rinsed apparatus. Because of differences among instruments, it is impossible to formulate detailed operating instructions. Follow recommendations of the manufacturer for selecting proper photocell and wavelength, for adjusting slit width and sensitivity, for appropriate fuel and oxidant pressures, and for the steps for warm-up, correcting for interferences and flame background, rinsing of burner, igniting sample, and measuring emission intensity.

1. Calibrate the instrument.

2. Analyze the samples.

3. Dilute with 1:1 extract:DI water solution and reanalyze any samples for which the concentration exceeds the calibration range and record aliquot and diluted volumes: K^+ [14-D] and [14-E]; Na^+ [15-D] and [15-E].

4. Record results for K^+ [14-F] and Na^+ [15-F]. Analyze Ca^{2+} and Mg^{2+} by ICP or AA and Al^{3+} by ICP.

13.7 Calculations

NOTE: Designations within the square brackets, [ ], represent the form number and column in which the data are entered on forms 12, 13, 14, 15, 16, and 1 (Appendix B, Figures B-35, B-36, B-37, B-38, B-39, and B-9).

Recovered Extract Volume = (Final weight − Tare weight) + Density (data from Section 11.6.2, Step 3.)

Final Extract Volume [12-C], [13-C], [14-C], [15-C], or [16-C] = Final wt. (g) − Tare wt. (g) + 1.0105

Exch. Cation (meq/100 g) = {[inst. reading] × ([total dil. vol.] + [aliq. vol.]) × [final extract vol.] × 1L + 1000 mL × 100 × meq + at. wt. (mg) × 1} + {[sample wt.] × (1 - [Moist]) + (100 + [Moist])}

CA_CL [12-G] = {[12-F] × ([12-E] + [12-D]) × [12-C] × 0.1 × 0.0499 × 1} + {[12-B] × (1 - [1-D]) + (100 + [1-D])}

MG_CL [13-G] = {[13-F] × ([13-E] + [13-D]) × [13-C] × 0.1 × 0.0822 × 1} + {[13-B] × (1 - [1-D]) + (100 + [1-D])}

K_CL (14-G] = {[14-F] × ([14-E] + [14-D]) × [14-C] × 0.1 × 0.0255 × 1} + {[14-B] × (1 - [1-D]) + (100 + [1-D])}

NA_CL [15-G] = {[15-F] × ([15-E] + [15-D]) × [15-C] × 0.1 × 0.0435 × 1} + {[15-B] × (1 - [1-D]) + (100 + [1-D])}

AL_CL [16-G] = {[16-F] × ([16-E] + [16-D]) × [16-C] × 0.1 × 0.1112 × 1} + {[16-B] × (1 - [1-D]) + (100 + [1-D])}

13.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water*, D1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Fassel, V. A. 1982. Analytical Spectroscopy with Inductively Coupled Plasma Present Status and Future Prospects. In: *Recent Advances in Analytical Spectroscopy*. Pergamon Press, New York, New York.

U.S. Environmental Protection Agency. 1983. *Methods for Chemical Analysis of Water and Wastes, Method 200.0, Atomic Absorption Methods; and Method 200.7, Inductively Coupled Plasma-Atomic Emission Spectrometric Method for the Trace Element Analysis of Water and Wastes.* EPA/600/4-79/020. U.S. Environmental Protection Agency, Cincinnati, Ohio.

14.0 *Exchangeable Cations in Calcium Chloride for Lime and Aluminum Potential*

14.1 Overview

Lime and aluminum potential are related to the concentrations of calcium (Ca^{2+}) and aluminum (Al^{3+}), respectively, that are extracted from a soil sample by a dilute calcium chloride ($CaCl_2$) solution. Lime potential is defined as pH − 1/2 pCa. The p-function is defined as the negative logarithm (base 10) of the molar concentration of that species, or: $pX = -\log [X]$. The advantage of using the p-function is that concentration information is available in terms of small positive numbers. Aluminum potential, K_{Al}, is defined as: $K_A = 3pH - pAl$.

The pH value determined in this method should be between the two pH values determined for each soil sample (see Section 10.0). Extractable Mg^{2+}, K^+, and Na^+ are also determined for comparison to amounts determined in the cation exchange capacity (CEC) extracts (see sections 12.0 and 13.0). Fe^{3+} and Al^{3+} are determined for comparison to amounts obtained by the extractable iron and aluminum procedures in Section 16.0.

14.1.1 Summary of Method

The procedure involves extraction of soil with 0.002 M $CaCl_2$. The soil-to-solution ratio is 1:2 for mineral soils and 1:10 for organic soils. The pH is determined using a pH meter and a combination electrode (see Section 10.0).

Atomic absorption spectroscopy (AA) can be used to measure calcium, magnesium, potassium, and sodium. A light beam from a hollow cathode lamp, the cathode of which is made of the element to be determined, is directed through the flame into a monochromator and onto a detector that measures the amount of light passing through the flame. Absorption depends upon the presence of free, unexcited, ground state atoms in the flame. Since the wavelength of the light beam is characteristic only of the cation being determined, the light energy absorbed by the flame is a measure of the concentration of that cation in the extract. A complete discussion of AA methods is provided in Appendix C.

Inductively coupled plasma spectroscopy (ICP) may be used to determine calcium, magnesium, sodium, iron, and aluminum. Samples are nebulized to produce an aerosol. The aerosol is transported by an argon carrier stream to an inductively coupled argon plasma, which is produced by a radio frequency generator. In the plasma (which is at a temperature of 6,000 to 10,000 °K) the analytes in the aerosol are atomized, ionized, and ionic emission spectra is produced. The spectra from all analytes are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed by a computer system. The signal is proportional to the analyte concentration and is calibrated by analyzing a series of standards (U.S. Environmental Protection Agency [USEPA], 1983; Fassel, 1982). A thorough discussion of ICP methods is provided in Appendix D.

Emission spectroscopy (ES) can be used to measure potassium and sodium. The sample is aspirated into a gas flame and excitation is carried out under carefully controlled and reproducible conditions. The desired spectral line is isolated by the use of interference filters or by a suitable slit arrangement in light-dispersing devices such as prisms or gratings. The intensity of light is measured by a phototube potentiometer or other appropriate circuit. The intensity of light at the appropriate wavelength (e.g., 589 nm for Na^+) is approximately proportional to the concentration of the element. A discussion of ES methods is provided in Appendix E.

14.1.2 Interferences

Chemical and spectral interferences can contribute to inaccuracies in analyses of the extracts by AA, ICP, or ES. Analyses by ICP and ES are subject to physical interferences as well. Additional details of these interferences and means for their obviation, elimination, or compensation are provided in appendices C, D, and E.

Spectral interferences are generally caused by spectral overlap from another element or background contributions. These interferences can usually be corrected by monitoring and compensating for the effect of interfering elements, selecting another wavelength, correcting background effects, or using a narrower slit width.

Chemical interferences are often caused by the cations forming molecular compounds instead of dissociated ions. This interference, most pronounced with the multivalent ions (such as Ca^{2+}, Mg^{2+}, and especially Al^{3+}), is negligible with the ICP technique. This interference is often corrected by the addition of lanthanum or lithium or by the avoidance of anions such as sulfate and phosphate.

The most common physical interference in the analysis of soils exchange solutions is salt build-up clogging the burner or nebulizer. Although dilution will reduce this problem, it will also change the matrix and any effect it may have on the instrument read-out.

Matrix effects are usually compensated by analyzing samples, and all calibration standards, reagent blanks, and quality control (QC) standards in the same matrix. Matrix effects may be tested by serial dilutions, spiked additions, and comparison with an alternative method of analysis. When the matrix effects are significant and cannot be readily corrected, the analyses must be performed by standard additions (see appendices C and D).

Soils high in salts, especially sodium, may interfere with the pH reading and the electrode response time. Clay particles may clog the liquid junction of the pH reference electrode, slowing the electrode response time; thoroughly rinse the electrode with deionized (DI) water between sample readings to avoid this problem. Wiping the electrode dry with cloth, laboratory tissue, or similar materials or removing the electrode from solution when the meter is not on standby may cause electrode polarization.

The initial pH of a nonalkaline soil will usually be as much as 0.5 pH unit greater than the pH taken after the sample has set for 30 minutes or longer. The pH can vary as much as 1.0 pH unit between the supernatant and soil sediment. Always place the electrode junction at the same distance (approximately 3 mm) above the surface of the soil sediment to maintain uniformity in pH readings.

14.1.3 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids should be restricted to a fume hood. Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

Follow the safety precautions of the manufacturer when operating instruments. Gas cylinders should always be chained or bolted in an upright position.

14.2 Sample Collection, Preservation, and Storage

A subsample is taken from the bulk soil sample after it has been air dried, homogenized, and tested for moisture content (see sections 4.0 and 8.0). Samples should be stored at 4 °C until ready for analysis. Preparation of the extraction aliquot is described in Section 14.6.1.

14.3 Equipment and Supplies

14.3.1 Equipment Specifications

1. Atomic absorption spectrophotometer, single- or dual-channel, single or double-beam, with grating monochromator, photomultiplier detector, adjustable slits, wavelength range of 190 to 800 nm, with a strip chart recorder and burner, as recommended by the instrument manufacturer (for certain elements, nitrous oxide burner required; hollow cathode lamps, single element lamps preferred, but multielement lamps acceptable; electrodeless discharge lamps may be used also).

2. Inductively coupled plasma atomic emission spectrometer, computer-controlled, with background correction capability.

3. Emission spectrometer, either direct-reading or internal-standard type; *or* atomic absorption spectrometer in flame emission mode.

4. Digital pH/ millivolt (mV) meter, capable of measuring pH to ±0.01 pH unit and potential to ±1 mV and temperature to ±0.5 °C. The meter must also have automatic temperature compensation capability (Orion Model 611 or equivalent).

5. A combination pH electrode, made of high quality, low-sodium glass. At least two electrodes, one a backup, should be available. Geltype reference electrodes must *not* be used; an Orion Ross combination pH electrode or equivalent with a retractable sleeve is recommended.

14.3.2 Apparatus

1. Shaker.

2. Centrifuge.

3. Balance, capable of weighing to 0.01 g.

4. Glass stirring rods.

5. Volumetric pipets, volumes as needed.

6. Volumetric flasks, volumes as needed.

7. Balance calibration weights, 3-5 weights covering expected range.

14.3.3 Reagents and Consumable Materials

1. Stock calcium chloride solution (1.0 M $CaCl_2$)--Dissolve 55.49 g anhydrous reagent grade $CaCl_2$ or 73.51 g $CaCl_2 \cdot 2H_2O$ in DI water and dilute to 500 mL.

2. Calcium chloride ($CaCl_2$) 0.002 M--Dilute 4 mL 1.0 M $CaCl_2$ to 2.0 L with DI water. If the pH of this solution is not between 5 and 6.5, adjust the pH by addition of dilute HCl or saturated $Ca(OH)_2$.

3. Calibration standards (Ca^{2+}, Mg^{2+}, K^+, Na^+, Al^{3+}, and Fe^{3+}).

4. pH calibration buffers (pH 4.0, 7.0, and 10.0)--Commercially available pH calibration buffers (National Bureau of Standards [NBS]-traceable) at pH values of 4.0 and 7.0 (two sets from different sources for calibration and quality control checks).

5. Potassium chloride (3M)--Dissolve 224 g KCl in DI water and dilute to 1 L.

6. Potassium chloride (0.1 M).

7. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

8. Bottles, linear polyethylene (LPE), with cap: 25-mL for mineral soil; 50-mL for organic soil.

9. Tubes, glass, 25-mL, centrifuge or culture, with caps.

10. Filter, membrane, 0.45-μm pore.

11. Weighing pans, disposable.

12. Forms--Form 18, pH in 0.002 M calcium chloride, Form 19, calcium in 0.002 M calcium chloride, Form 20, magnesium in 0.002 M calcium chloride, Form 21, potassium in 0.002 M calcium chloride, Form 22, sodium in 0.002 M calcium chloride, Form 23, iron in 0.002 M calcium chloride, Form 24, aluminum in 0.002 M calcium chloride, Form QC-18, Form QC-19, Form QC-20, Form QC-21, Form QC-22, Form QC-23, and Form QC-24 (Appendix B, figures B-45 through B-58, respectively).

14.4 Calibration and Standardization

Within each class of instruments (AA, ICP, and ES), the calibration procedure varies slightly. Curves must be linear and cover the range of concentrations measured in the extract. Calibration standards for Ca^{2+} determinations are prepared using DI water, while calibration standards for Mg^{2+}, Na^+, K^+, Al^{3+}, and Fe^{3+} are prepared in the 0.002 M $CaCl_2$ solution. Detailed calibration procedures for AA, ICP, and ES are provided in appendices C, D, and E, respectively; pH meter calibration is detailed in Section 10.0, and calibration of balances is described in Appendix A.

14.5 Quality Control

Log all QC data on forms QC-18 through QC-24 (Appendix B, figures B-52 through B-58, respectively); refer to Section 3.0 for additional information concerning these internal quality control checks.

Calibration Blanks--Calibration blanks for each cation should be analyzed before the initial sample analysis, at specified intervals thereafter (e.g., after every ten samples) and after the last sample of each batch. For Mg^{2+}, K^+, and Na^+, the calibration blank prepared (0.002 M $CaCl_2$ solution) should be 0.05 mg/L or less. For Ca^{2+}, the calibration blank (DI water) should be 0.500 mg/L or less. For the Fe^{3+} and Al^{3+} cations, blanks (0.002 M $CaCl_2$ solution) should be 0.10 mg/L or less. If any blank is higher than these limits, check the system and reanalyze all samples since the last acceptable calibration blank.

Reagent Blanks--Three reagent blanks are analyzed with each batch of samples for each cation. Reagent blanks consist of the 0.002 M $CaCl_2$ extraction solution passed through the analytical procedure without any soil being present. The reagent blank for Ca^{2+} should be between 76 and 84 mg/L. The pH blank should be between 4.5 and 7.5 pH units. Each of the other reagent blanks should be less than or equal to the contract-required detection limit (CRDL) in Table 3-2.

Replicates--One sample from each batch should be extracted and analyzed in duplicate for all six cations. Triplicate analyses of the duplicate sample for each batch is required for pH. The percent relative standard deviation (%RSD) should meet the limits outlined in Table 3-3.

QC Standards--One detection limit quality control check standard (DL-QCCS) should be analyzed for each cation with each batch of samples. The DL-QCCS standard is prepared in 0.002 M $CaCl_2$. Recommended concentration of Mg^{2+}, K^+, and Na^+ in the DL-QCCS is 0.15 mg/L each; concentration of Ca^{2+} is 0.50 mg/L; concentration of Fe^{3+} and Al^{3+} is 1.0 mg/L each. Measured values for Ca^{2+} should be 76 to 84 mg/L; measured values for each of the other cations should be within 20 percent of the known concentration.

QCCSs of concentrations at about mid-calibration range of the samples being analyzed should be measured for each cation before the first sample, at specified intervals thereafter (e.g., every tenth sample) and after the last sample of each batch of samples for both exchanges. Measured values for each QCCS should be within 10 percent of the known value.

A pH 4.00 standard, from a different preparation source or lot number than that used for the calibration, is used as the QCCS for pH. Each reading for the pH QCCS should fall between 3.95 and 4.05 pH units.

Spike Solution--For each batch of samples, a spike solution should be analyzed three times for Ca^{2+} content. The spike solution consists of the 0.002 M $CaCl_2$ extraction solution that is used for the extraction of all six cations. Measured values for the Ca^{2+} in the spike solution should be 76 to 84 mg/L Ca^{2+}.

Matrix Spike--For each batch of soils, the extract from one sample is spiked with a known concentration for each cation being determined. The known spike value should be 1.5 to 3.0 times the measured concentration, or ten times the CRDL, whichever is greater. Calculated recovery of the spike should be 90 to 110 percent of the known concentration of the spike. No spike is required for the pH determination.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy windows provided by the QA manager.

14.6 Procedure

Before proceeding with the analytical procedure, the analyst should be certain that all QC procedures have been implemented, all labware has been properly cleaned, and valid instrumental detection limits (IDLs) have been obtained, as outlined in Section 3.0 and Appendix A. Detailed procedures for AA, ICP, and ES are provided in appendices C, D, and E.

NOTE: Figures within the square brackets, [ ], represent the form number and column in which the data are entered.

14.6.1 Extraction

1. For mineral soils, weigh 20.00 g air-dry soil to nearest 0.01 g, and for organic soils, weigh 8.00 g air-dry soil to nearest 0.01 g. Record: pH [18-B]; Ca^{2+} [19-B]; Mg^{2+} [20-C]; K^+ [21-C]; Na^+ [22-C]; Fe^{3+} [23-C]; and Al^{3+} [24-B].
2. Place weighed samples in sample tube and add 40.0 mL of 0.002 M $CaCl_2$ to mineral soils and 80.0 mL of 0.002 M $CaCl_2$ to the organic soils. Record: pH [18-C]; Ca^{2+} [19-C]; Mg^{2+} [20-C]; K^+ [21-C]; Na^+ [22-C]; Fe^{3+} [23-C]; and Al^{3+} [24-C].
3. Stir each sample thoroughly to assure it is completely wetted with the 0.002 M $CaCl_2$ extract solution.
4. Securely cap the sample tubes, place the closed sample tubes securely in a horizontal position on a mechanical shaker and shake for at least one hour, let stand overnight, and resuspend prior to centrifugation.
5. Decant about half the liquid into a 50-mL centrifuge tube, saving the remainder of the liquid and wet soil for the pH determination.
6. Centrifuge the samples in the sample tubes for 5 minutes.
7. Filter the supernatant using a 0.45-µm filter into a clean sample tube and refrigerate at 4 °C until analyses are made for Ca^{2+}, Mg^{2+}, K^+, Na^+, Fe^{3+}, and Al^{3+}.

14.6.2 Cation Determination

1. Determine the concentration of the six cations using appropriate instrumentation:

   AA - Ca^{2+}, Mg^{2+}, K^+, and Na^+
   ICP - Ca^{2+}, Mg^{2+}, Na^+, Fe^{3+}, and Al^{3+}
   ES - K^+ and Na^+

2. Dilute any sample with high concentration for the respective analyte measured above the linear dynamic calibration range of the instrument.

   NOTE: When analyzing for Mg^{2+}, K^+, Na^+, Fe^{3+}, and Al^{3+}, a maximum dilution of 1:1 (one part extract:one part DI water) is permissible prior to preliminary analysis.

3. Log the aliquot volume, diluted volume, and measured diluted concentration (mg/L) for the six cations: Ca^{2+} [19-D], [19-E], [19-F]; Mg^{2+} [20-D], [20-E], [20-F]; K^{+} [21-D], [21-E], [21-F]; Na^{+} [22-D], [22-E], [22-F]; Fe^{3+} [23-D], [23-E], [23-F]; and Al^{3+} [24-D], [24-E], [24-F].

14.6.3 pH Determination

1. Allow the suspension to settle for at least 1 minute. Immerse the pH electrode into the suspension so that the reference junction is below the surface of the solution, but above the sediment.

2. Read the pH to the nearest 0.01 pH unit and record: [19-D].

3. After measurements are completed, store the electrode in 0.1 M KCl storage solution. Do not let the sensing element and reference junction dry out. The level of the storage solution should be one inch below the filling solution level to prevent influx of the storage solution. Check periodically that the electrode reservoir is full of filling solution.

14.7 Calculations

NOTE: No calculations are required in order to obtain pH values; the final value is [18-D]. Designations within the square brackets, [ ], represent the form number and column in which the data are entered on forms 19, 20, 21, 22, 23, 24, and 1 (Appendix B, figures B-46, B-47, B-48, B-49, B-50, B-51, and B-9).

Cations (meq/100 g) = {[inst. reading] × ([total dil. vol.] ÷ [aliq. vol.]) × [final extract vol.] × 1L ÷ 1000 mL × 100 g × (meq ÷ at. wt. (mg)) × 1} ÷ {[sample wt.] × (1 - [Moist]) ÷ (100 + [Moist])}

CA_CL2 [19-G] = {[19-F] × ([19-E] ÷ [19-D]) × [19-C] × 0.1 × 0.0499 × 1} ÷ {[19-B] × (1 - [1-D]) ÷ (100 + [1-D])}

MG_CL2 [20-G] = {[20-F] × ([20-E] ÷ [20-D]) × [20-C] × 0.1 × 0.0823 × 1} ÷ {[20-B] × (1 - [1-D]) ÷ (100 + [1-D])}

K_CL2 [21-G] = {[21-F] × ([21-E] ÷ [21-D]) × [21-C] × 0.1 × 0.0252 × 1} ÷ {[21-B] × (1 - [1-D]) ÷ (100 + [1-D])}

NA_CL2 [22-G] = {[22-F] × ([22-E] ÷ [22-D]) × [22-C] × 0.1 × 0.0435 × 1} ÷ {[22-B] × (1 - [1-D]) ÷ (100 + [1-D])}

FE_CL2 [23-G] = {[23-F] × ([23-E] ÷ [23-D]) × [23-C] × 0.1 × 0.0537 × 1} ÷ {[23-B] × (1 - [1-D]) ÷ (100 + [1-D])}

AL_CL2 [24-G] = {[24-F] × ([24-E] ÷ [24-D]) × [24-C] × 0.1 × 0.1112 × 1} ÷ {[24-B] × (1 - [1-D]) ÷ (100 + [1-D])}

14.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.10, Standard Specification for Reagent Water,* D-1193-77 (reapproved 1983). American Society for Testing and Materials, Philadelphia, Pennsylvania.

Fassel, V. A. 1982. Analytical Spectroscopy with Inductively Coupled Plasma Present Status and Future Prospects. In: *Recent Advances in Analytical Spectroscopy.* Pergamon Press, New York, New York.

U.S. Environmental Protection Agency. 1983 (revised). *Methods for Chemical Analysis of Water and Wastes.* Method 200.0, Atomic Absorption Methods, and Method 200.7, Inductively Coupled Plasma Atomic Emission Spectrometric Method for the Trace Element Analysis of Water and Wastes. EPA-600/4-79/020. U.S. Environmental Protection Agency, Cincinnati, Ohio.

15.0 Exchangeable Acidity

15.1 Overview

Exchangeable acidity is a fairly arbitrary quantity composed of four types of acidity:

1) H^+ derived from hydrolysis of Al^{3+},
2) hydrolysis of nonexchangeable Al,
3) weakly acidic groups predominantly on organic matter, and
4) exchangeable H.

The method most frequently used to determine exchangeable acidity involves treatment of the soil sample with a barium chloride triethanolamine ($BaCl_2$-TEA) solution buffered to pH 8.2 followed by titration of the extracted solution. This method measures total potential acidity (Thomas, 1982).

15.1.1 Summary of Method

Exchangeable acidic ions are extracted from a soil sample using a mechanical extractor with a $BaCl_2$-TEA extracting solution. The excess reagent in the extract is back-titrated with HCl. Results are expressed as milliequivalents (meq) exchangeable acidity per 100 g soil.

15.1.2 Interferences

Atmospheric carbon dioxide can interfere with the $BaCl_2$-TEA extraction. The use of buffered solution is meant to minimize this effect. Use of automated equipment minimizes the effects of variation in technique.

15.1.3 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids and ammonium hydroxide solutions should be restricted to a fume hood.

Follow the safety precautions of the manufacturer when operating the instruments.

15.2 Sample Collection, Preservation, and Storage

A subsample is taken from the bulk soil sample after it has been air dried, homogenized, and tested for moisture content (see sections 4.0 and 8.0). Samples should be stored at 4 °C until ready for analysis. Preparation of the soil extractions is described in sections 15.6.1 and 15.6.2.

15.3 Equipment and Supplies

15.3.1 Apparatus and Equipment

1. Balance, capable of weighing to 0.01 g.

2. Mechanical extractor, 24-place, manufactured by Centurion, Inc. or equivalent (see Figure 11-1).

3. Pipettors, volume adjustable to 25 mL (2 required).

4. Erlenmeyer flasks, 250-mL and 125-mL.

5. Reciprocating shaker.

6. Volumetric flasks, volumes as needed.

7. Automatic titrator.

8. Digital pH/ millivolt (mV) meter, capable of measuring pH to ±0.01 pH unit and potential to ±1 mV and temperature to ±0.5 °C. The meter must also have automatic temperature compensation capability (Orion Model 611 or equivalent).

9. A combination pH electrode, made of high quality, low-sodium glass. At least two electrodes, one as a backup, should be available. Gel-type reference electrodes must *not* be used; an Orion Ross combination pH electrode or equivalent with a retractable sleeve is recommended.

10. Balance calibration weights, 3-5 weights covering expected range.

15.3.2 Reagents

1. Buffer solution for mineral soils [0.5 N $BaCl_2$-0.10 N $N(CH_2CH_2OH)_3$]--Dissolve 61.07 g $BaCl_2 \cdot 2H_2O$ and 14.92 g TEA in CO_2-free, deionized (DI) water and dilute to 1.00 L. Adjust pH to 8.2 with 10 percent HCl. Protect solution from CO_2 contamination by attaching a drying tube containing Ascarite to the air intake of the storage vessel.

2. Buffer solution for organic soils [0.5 N $BaCl_2$-0.2 N $N(CH_2CH_2OH)_3$]--Dissolve 61.07 g $BaCl_2 \cdot 2H_2O$ and 29.8 g TEA in CO_2-free, DI water and dilute to 1.00 L. Adjust pH to 8.2 with 10 percent HCl. Protect solution from CO_2 contamination by attaching a drying tube containing Ascarite to the air intake of the storage vessel.

3. Replacement solution (0.5 N with respect to $BaCl_2$)--Dissolve 61.07 g $BaCl_2 \cdot 2H_2O$ with 5 mL of the appropriate $BaCl_2$-TEA buffer solution and dilute to 1.00 L with DI water.

4. Hydrochloric acid, concentrated (12 M HCl)--Ultrapure, Baker Instra-Analyzed or equivalent.

5. Hydrochloric acid (1 percent v/v)--Add 5 mL concentrated HCl to 495 mL DI water.

6. Hydrochloric acid (0.100 N, standardized)--Dilute 8.32 mL concentrated HCl to 1.00 L with DI water. Standardize against reagent grade sodium carbonate to methyl orange endpoint. This may also be purchased as certified, standardized 0.100 N HCl.

7. Hydrochloric acid (0.050 N, standardized)--Dilute 4.15 mL concentrated HCl to 1.00 L with DI water. Standardize against reagent grade sodium carbonate to methyl orange endpoint. This may also be purchased as certified, standardized 0.050 N HCl.

8. pH calibration buffers (pH 4.0, 7.0, and 10.0)--Commercially available pH calibration buffers (National Bureau of Standards [NBS]-traceable) at pH values of 4.0, 7.0, and 10.0 (two sets from different sources for calibration and quality control checks).

9. Washed analytical filter pulp, Schleicher and Schuell, No. 289 (see Section 11.6.1 for washing procedure). Commercial pulps are often contaminated and will have to be washed.
10. Ascarite.
11. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

15.3.3 Consumable Materials

1. Syringes, 60-mL, one sample tube and one extraction syringe per sample.
2. Stirring rods, glass; one per sample.
3. Tubes, glass, 25-mL, centrifuge or culture, with caps.
4. Bottles, polyethylene, 25-mL, optional.
5. Weighing pans, disposable.
6. Forms--Form 17, barium chloride-TEA acidity and Form QC-17 (Appendix B, figures B-59 and B-60).

15.4 Calibration and Standardization

Calibrate the titrator for the volume of solution to be delivered. Calibrate the pH electrode by using two pH buffers that bracket the desired endpoint (see Section 10.4). Normalities of titrants (label values) should be checked weekly during use. If the check normality differs from the label value by more than 5 percent, perform two additional checks. Calculate the mean normality from the three checks; this mean becomes the label value used in the acidity calculations. The same standard titrant must be used for the entire batch of samples.

Balance calibration is detailed in Appendix A.

15.5 Quality Control

Log all quality control (QC) data on Form QC-17 (Appendix B, Figure B-60; refer to Section 3.0 for additional information regarding these internal quality control checks.

Calibration Blanks--Calibration blanks should be analyzed before the initial sample analysis, at specified intervals thereafter (e.g., after every ten samples) and after the last sample of each batch. The calibration blank should be composed of 20 mL of the buffer solution, 40 mL of the replacement solution, and 100 mL of DI water. The calibration blank should contain between 1.3 and 1.8 meq for mineral soils. If any blank is outside these limits, check the system and reanalyze all samples since the last acceptable calibration blank.

Reagent Blanks--Three reagent blanks, carried through the extraction procedure, are analyzed with each batch of samples. This composition will result in a solution composition of between 1.3 and 1.8 meq for mineral soils. The mean of the reagent blank values is used in the acidity calculation.

Replicates--One sample from each batch should be weighed, extracted, and analyzed in duplicate. The percent relative standard deviation (%RSD) should meet the limits listed in Table 3-3.

QC Standards--One detection limit quality control check standard (DL-QCCS) should be analyzed with each batch of samples. Measured values should be within 20 percent of the known value of the DL-QCCS standard.

QCCSs of concentrations at about the mid-calibration range of the samples being analyzed should be measured before the first sample, at specified intervals thereafter (e.g., every tenth sample) and after the last sample of each batch. Measured values for each QCCS should be within 10 percent of the known value.

Prepare the DL-QCCS and QCCS as follows: mix 20 mL of the buffer solution, 40 mL of the replacement solution, and 100 mL of DI water; for the DL-QCCS, add sufficient acid (HCl) to neutralize approximately 0.015 meq (a suggested addition of 0.3 mL of 0.050 N HCl is appropriate); for the QCCS, neutralize approximately 20 percent of the buffer to reach the mid-calibration range (a suggested addition of 8 mL of 0.050 N HCl is appropriate for mineral soils and 8 mL of 0.1 N HCl is appropriate for organic soils).

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy windows provided by the quality assurance (QA) manager.

15.6 Procedure

Exchangeable acidity analyses should not be done until the samples are properly prepared, the air-dry moisture is determined, and valid instrumental detection limits (IDLs) (see sections 3.0, 4.0, and 8.0), are determined. Data should be logged following the procedures described in Section 3.0.

NOTE: Figures within the square brackets, [ ], represent the form number and column in which the data are entered.

15.6.1 Mineral Soils

1. Tightly compress a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger. (To modify the plunger, remove the rubber portion and cut off the plastic protrusion.) Tap the plunger and syringe assembly on a tabletop several times.

2. Weigh 2.00 g air-dry mineral sample into tube and record exact weight [17-B]. Place sample tube in upper disc of extractor and connect to inverted extraction syringe. The plunger of this syringe is inserted in the slot of the stationary disc of the extractor. Attach pinch clamp to delivery tube of syringe barrel. Add 10.00 mL $BaCl_2$-TEA *buffer* solution for mineral soils to the sample. Stir the sample mixture with a glass stirring rod for 10 seconds. Leave stirring rod in syringe. Allow sample to stand for 30 minutes.

3. Set extractor for a 30-minute rate and extract until 0.5 to 1.0 cm of solution remains above each sample. If necessary, turn off extractor to prevent soil from becoming dry.

4. Add a second 10.00-mL aliquot of $BaCl_2$-TEA *buffer* solution and continue extracting until nearly all solution has been pulled through sample. Add *replacement* solution from pipettor in two 20-mL aliquots, passing the first aliquot through the sample before adding

the next. Total time for replacement should be approximately 30 minutes. Quantitatively transfer extract to an Erlenmeyer flask. Record the total volume of buffer plus replacement solutions [17-C].

NOTE: DI water may be used at this point to aid in the quantitation transfer. The final volume of DI water should be 100 mL - see Step 5.

5. *Titration*--Add 100 mL DI water to extract in Erlenmeyer flask. Use an automatic titrator to titrate with 0.050 N HCl to a 4.60 pH endpoint. Record volume [17-D] and normality [17-E] of titrant. If the volume of titrant of any sample is less than 5 percent of that measured for the blank, resolve the problem before further analysis.

15.6.2 Organic Soils

1. Tightly compress a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger. (To modify the plunger, remove the rubber portion and cut off the plastic protrusion.) Tap the plunger and syringe assembly on a tabletop several times.

2. Weigh 2.00 g of air-dry organic sample soil into small glass tube and record exact weight [17-B]. Add 5.00 mL $BaCl_2$-TEA *buffer* solution for organic soils to the sample, cap, and shake the tube and contents for 1 hour on a reciprocating shaker. Place sample tube in upper disc of extractor and connect to inverted extraction syringe, with the syringe plunger inserted in the slot of the stationary disc of the extractor. Attach pinch clamp to delivery tube of syringe barrel. Quantitatively transfer contents of small glass tube to sample tube with 5.00 mL *buffer* solution.

   NOTE 1: Five to 10 mL of buffer solution may be used to transfer soil to syringe - see Step 4.

   NOTE 2: Some organic soils have very high acidity, which may require reducing the amount of soil to 1.00 g to stay in the mid-range of the titration procedure; note and flag (see Table 3-4) all data appropriately.

3. Set extractor for a 30-minute rate and extract until 0.5 to 1.0 cm of solution remains above each sample. If necessary, turn off extractor to prevent soil from becoming dry.

4. Add a second 10.00-mL aliquot of $BaCl_2$-TEA *buffer* solution and continue extracting until nearly all solution has been pulled through sample. Add *replacement* solution from pipettor in two 20-mL aliquots, passing the first aliquot through the sample before adding the next. Total time for replacement should be approximately 30 minutes. Quantitatively transfer extract to an Erlenmeyer flask. Record the total volume of buffer plus replacement solutions [17-C].

   NOTE 1: If 10-mL was used in Step 2, then 5 mL must be used here. Total buffer used must equal 20.00 mL. A second extraction is essential.

   NOTE 2: DI water may be used at this point to aid in the quantitative transfer. The final volume of DI water added must equal 100 mL (see Step 5).

5. *Titration*--Add 100 mL DI water to extract in Erlenmeyer flask. Use an automatic titrator to titrate with 0.100 N HCl to a 4.60 pH endpoint. Record volume [17-D] and normality

[17-E] of titrant. If the volume of titrant of any sample is less than 5 percent of that measured for the blank, resolve the problem before further analysis.

15.7 Calculations

NOTE: Designations within the square brackets, [ ], represent the form number and column in which the data are entered on forms 17 and 1 (Appendix B, Figures B-59 and B-1).

Exch. Acidity (meq/100 g) = {([Mean Blank] (mL)] - [Titrant (mL)]) × [Normality of Titrant] × 1} + {[sample wt.] × (1 - [Moist]) + (100 + [Moist])}

AC_BACL [17-F] = {([Mean Blank] - [17-D]) × [17-E] × 1} + {[17-B] × (1 - [1-D]) + (100 + [1-D])}

15.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water,* D-1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Thomas, G. W. 1982. Exchangeable cations. In: A. L. Page, Miller, R. H., Reeney, D. R. (eds.) *Methods of soil analysis.* Agronomy 9, Partz. American Society of Agronomy, Madison Wisconsin.

16.0 Extractable Iron, Aluminum, and Silicon

16.1 Overview

Iron and aluminum are extracted from soil by sodium pyrophosphate, citrate-dithionite, and acid-oxalate solutions. According to the Johnson and Todd (1983) iron and aluminum speciation scheme, the pyrophosphate extract contains organically bound iron and aluminum, the citrate-dithionite extract contains non-silicate Fe^{3+} and Al^{3+}, and the acid-oxalate extract contains organic and amorphous oxides of Fe^{3+} and Al^{3+}. The exchangeable Al^{3+} from the unbuffered NH_4Cl extract (see Section 13.0) is more indicative of readily available Al^{3+} under field conditions. The Fe^{3+} and Al^{3+} values from the pyrophosphate, acid-oxalate, and citrate-dithionite extracts relate directly to the sulfate adsorption capacity and have been used as an indication of this property (Fernandez, 1983). Silicon is extracted with the acid oxalate.

16.1.1 Summary of Method

Each of three portions of a soil sample is treated with a different solution to extract iron and aluminum. The three extracting solutions are 0.1 M sodium pyrophosphate, a sodium citrate-sodium dithionite solution, and an oxalic acid-ammonium oxalate solution. After extraction, the three solutions are analyzed for iron, aluminum, and silicon by inductively coupled plasma spectroscopy (ICP).

In ICP, samples are nebulized to produce an aerosol. The aerosol is transported by an argon carrier stream to an inductively coupled argon plasma, which is produced by a radio frequency generator. In the plasma (which is at a temperature of 6,000 to 10,000 °K) the analytes in the aerosol are atomized, ionized, and ionic emission spectra is produced. The spectra from all analytes are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed by a computer system. The signal is proportional to the analyte concentration and is calibrated by analyzing a series of standards (U.S. Environmental Protection Agency [USEPA], 1983; Fassel, 1982). A thorough discussion of ICP methods is provided in Appendix D.

16.1.2 Interferences

Chemical, spectral, and physical interferences can contribute to inaccuracies in analysis of the extracts by ICP. Additional details of these interferences and means for their obviation, elimination, or compensation are provided in Appendix D.

Spectral interferences are generally caused by spectral overlap from another element or background contributions. These interferences can usually be corrected by monitoring and compensating for the effect of interfering elements, selecting another wavelength, correcting background effects, or using a narrower slit width.

Chemical interferences are often caused by the cations forming molecular compounds instead of dissociated ions. This interference, most pronounced with the multivalent ions (such as Al^{3+}), is negligible with the ICP technique. This interference is often corrected by the addition of lanthanum or lithium or by the avoidance of anions such as sulfate and phosphate.

The most common physical interference in the analysis of soils exchange solutions is salt build-up clogging the burner or nebulizer. Although dilution will reduce this problem, it will also change the matrix and any effect it may have on the instrument read-out.

Matrix effects are usually compensated for by analyzing samples, and all calibration standards, reagent blanks, and quality control (QC) standards in the same matrix. Matrix effects may be tested by serial dilutions, spiked additions, and comparison with an alternative method of analysis. When the matrix effects are significant and cannot be readily corrected, the analyses must be performed by standard additions (see appendices C and D).

16.1.3 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids and hydroxide solutions should be restricted to a fume hood.

Follow the safety precautions provided by the manufacturer when operating instruments. Gas cylinders should be chained or bolted in an upright position.

16.2 Sample Collection, Preservation, and Storage

A subsample is taken from the bulk soil sample after it has been air dried, homogenized, and tested for moisture content (see sections 4.0 and 8.0). Samples should be stored at 4 °C until ready for analysis. Preparation of the soil extractions is described in sections 16.6.1, 16.6.2, and 16.6.3.

NOTE: The subsample may be ground to pass a No. 60 (U.S. No.) or No. 100 sieve, if desired.

16.3 Equipment and Supplies

16.3.1 Equipment Specifications

1. Inductively coupled plasma atomic emission spectrometer, computer-controlled, with background correction capability.

2. Digital pH/millivolt (mV) meter, capable of measuring pH to ±0.01 pH unit, potential to ±1 mv, and temperature to ±0.5 °C. The meter must also have automatic temperature compensation capability (Orion Model 611 or equivalent).

3. A combination pH electrode, made of high quality, low-sodium glass. At least two electrodes, one as a backup, should be available. Gel-type reference electrodes must *not* be used; an Orion Ross combination pH electrode or equivalent with a retractable sleeve is recommended.

16.3.2 Apparatus

1. Balance, capable of weighing to nearest 0.01 g.

2. Reciprocating box shaker.

3. Centrifuge.

4. Repipet or equivalent.
5. Fleakers, or equivalent glassware.
6. Volumetric pipets, volumes as needed.
7. Volumetric flasks, volumes as needed.
8. Balance calibration weights, 3-5 weights covering expected range.
9. Cardboard box, large enough to hold 250-mL bottle.

16.3.3 Reagents

16.3.3.1 Sodium Pyrophosphate Extraction--

1. National Bureau of Standards [NBS]-traceable pH buffers of pH = 7 and pH = 10.
2. Sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$), 0.1 M--Dissolve 446.1 g $Na_4P_2O_7 \cdot 10\ H_2O$ in deionized (DI) water. Dilute to 10 L. Adjust to pH 10.0 by dropwise additions of 1 N NaOH or 1 N H_3PO_4.
3. Sodium hydroxide (NaOH), 1 N--Dissolve 10 g NaOH in DI water. Dilute to 250 mL. Store in polyethylene container.
4. Phosphoric acid (H_3PO_4), concentrated.
5. Superfloc 16, 0.2 percent solution (v/v) in DI water (possible source: American Cyanamid Co., P.O. Box 32787, Charlotte, NC 28232; telephone: (800) 438-5615).
6. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

16.3.3.2 Citrate-Dithionite Extraction--

1. Sodium dithionite ($Na_2S_2O_4$).
2. Sodium citrate ($Na_3C_6H_5O_7 \cdot 5H_2O$).
3. Citrate-dithionite reagent--Dissolve 160 g sodium dithionite and 2,000 g sodium citrate into approximately 8 L of DI water. Dilute to 10 L. Store at 4 °C and use the same day.

   NOTE: This may require prolonged magnetic stirring or additional DI water to totally dissolve the salts.

4. Superfloc 16, 0.2 percent solution (v/v) in DI water.
5. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

16.3.3.3 Acid-Oxalate Extraction--

1. NBS-traceable pH buffers of pH = 4 and pH = 3 or pH = 2.

2. Ammonium oxalate [$(NH_4)_2C_2O_4 \cdot H_2O$].

3. Oxalic acid ($H_2C_2O_4 \cdot H_2O$).

4. Acid-oxalate reagent--Solution A: Dissolve 284 g ammonium oxalate [$(NH_4)_2C_2O_4 \cdot H_2O$] in DI water and dilute to 10 L. Solution B: Dissolve 252 g oxalic acid ($H_2C_2O_4 \cdot H_2O$) in DI water and dilute to 10 L. Mix four parts Solution A with three parts Solution B. Adjust pH to 3.0 by adding either Solution A or B.

5. Superfloc 16, 0.2 percent.

6. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

16.3.4 Consumable Materials

1. Centrifuge bottles, 250-mL, polypropylene.

2. Bottles, linear polyethylene (LPE), 25-mL.

3. ICP vials, provided by ICP manufacterer or clean 250-mL LPE bottles.

4. Weighing pans, disposable.

5. Forms--Form 25, pyrophosphate extractable iron, Form 26, pyrophosphate extractable aluminum, Form 27, acid oxalate extractable iron, Form 28, acid oxalate extractable aluminum, Form 29, acid oxalate extractable silicon, Form 30, citrate dithionite extractable iron, Form 31, citrate dithionite extractable aluminum, and forms QC-25 through QC-31 (Appendix B, figures B-61 through B-74).

6. Aluminum foil, heavy duty.

16.4 Calibration and Standardization

The matrix of the calibration standards should match the matrix of the soil extracts as closely as possible to assure maximum accuracy. Therefore, *it is highly recommended that the calibration standards be prepared with the extracting solution* rather than water as the diluent.

Calibrate the instrument by analyzing a calibration blank and a series of at least three standards within the linear range. A multielement standard may be prepared and analyzed. The concentration of standards must bracket the expected sample concentration; however, the linear range of the instrument should not be exceeded.

Detailed procedures for ICP calibration are given in Appendix D; pH meter calibration is discussed in Section 10.4; and calibration of balances is discussed in Appendix A.

16.5 Quality Control

Log all QC data on forms QC-25 through QC-31 (Appendix B, figures B-68 through B-74); refer to Section 3.0 for additional information concerning these internal quality control checks.

Calibration Blanks--Calibration blanks for both Fe^{3+} and Al^{3+} in the three extracts should be analyzed before the initial sample analysis, at specified intervals thereafter (e.g., after every ten samples) and after the last sample of each batch. Each blank should have a concentration of 0.50 mg/L or less.

Reagent Blanks--Three reagent blanks, carried through the extraction procedure, are analyzed with each batch of samples. Each blank should have a concentration of 0.50 mg/L or less.

Replicates--One sample from each batch should be extracted in duplicate for each of the three extracting solutions and analyzed for Fe^{3+} and Al^{3+} in each of the extracts and Si^{4+} in the acid-oxalate extract. The percent relative standard deviation (% RSD) should meet the limits listed in Table 3-3.

QC Standards--One detection limit quality control check standard (DL-QCCS) should be analyzed with each batch of samples for Fe^{3+} and Al^{3+} in each of the three extracts and for Si^{4+} in acid-oxalate solution. Concentrations of both Fe^{3+} and Al^{3+} in the three extraction solutions, as well as for Si^{4+} in acid-oxalate solution, should be within 1.00 to 1.50 mg/L. Measured results for the DL-QCCS should be within 20 percent of the known concentrations.

QCCSs of concentrations at about mid-calibration range of the samples being analyzed should be measured for both Fe^{3+} and Al^{3+} in each of the three extracts and Si^{4+} in the acid-oxalate solution. These measurements should be performed before the first sample, at specified intervals thereafter (e.g., every tenth sample) and after the last sample of each batch. Measured values for each QCCS should be within 10 percent of the known value.

Matrix Spike--For each batch of soils, each extract from one sample should be spiked with a known concentration for each variable being determined. The concentration of sample plus spike should be between 1.5 to 3 times the measured concentration of the sample. Calculated recovery of the spike should be 90 to 110 percent of the known concentration of the spike.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy windows provided by the quality assurance (QA) manager.

16.6 Procedure

Before proceeding with the analytical procedure, the analyst should be certain that all QC procedures have been implemented, all labware has been properly cleaned, and valid instrumental detection limits (IDLs) have been obtained, as outlined in Section 3.0 and Appendix A. Data should be logged following the procedures described in Section 3.0. Detailed procedures for ICP are given in Appendix D.

NOTE: Figures within the square brackets, [ ], represent the form number and column in which the data are entered.

16.6.1 Sodium Pyrophosphate Extraction

1. Place 2.00 g of air-dry mineral or organic soil into a 250-mL centrifuge bottle and record exact weight [25-B] and [26-B]. Add 200 mL 0.1 M $Na_4P_2O_7$, cap, and shake overnight (16 hours) on a reciprocating box shaker at approximately 1 to 2 cycles per second. The shaker should be properly ventilated to prevent heat buildup.

2. Remove centrifuge bottle from shaker. Add 4 mL of 0.2 percent Superfloc solution. Shake for 15 seconds and centrifuge for 10 minutes. Record total volume, 204 mL, used in the extraction [25-C] and [26-C].

3. Remove centrifuge bottle from centrifuge. Examine the supernatant for suspended clays. The supernatant may not be clear because the pyrophosphate solution is relatively viscous and the clays are sodium-saturated. If it is not, repeat Step 2 and the centrifugation until supernatant is clear.

4. Decant and save the supernatant. Store the supernatant at 4 °C prior to analysis.

5. Analyze for Fe^{3+} and Al^{3+} by ICP within 24 hours of completion of the extraction. Log the concentration in mg/L in [25-F] and [26-F].

6. Dilute any sample having a concentration above the linear dynamic calibration range of the instrument. Log the aliquot volume, diluted volume, and measured concentration in the diluted volume as follows: Fe^{3+}: [25-D], [25-E], [25-F]; Al^{3+}: [26-D], [26-E], [26-F].

16.6.2 Acid-Oxalate Extraction

This extraction is sensitive to light; therefore, it should be performed under conditions of darkness. Samples may be protected from light by wrapping bottles in heavy-duty aluminum foil.

1. Weigh 2.00 g of air-dry mineral or organic soil into 250-mL bottles and record exact weight [27-B], [28-B], and [29-B].

2. Add 200 mL of acid-oxalate reagent to the soil samples.

3. Place the 250-mL bottles in a container to protect from light and shake on a reciprocating box shaker for 4 hours at 1 to 2 cycles per second. Alternately, the reciprocating box shaker may be located in a light-protected area.

4. Add 4 mL of 0.2 percent Superfloc solution and centrifuge for 10 minutes. Log total solution, 204 mL, in [27-C], [28-C], and [29-C].

5. Transfer the clear supernatant liquid to vials.

6. Analyze for Fe^{3+}, Al^{3+}, and Si^{4+} by ICP.

7. Dilute any sample having a concentration above the linear dynamic calibration range of the instrument.

8. Log aliquot and diluted volume and measured concentration as follows: Fe^{3+}: [27-D], [27-E], [27-F]; Al^{3+}: [28-D], [28-E], [28-F]; Si^{4+}: [29-D], [29-E], [29-F].

16.6.3 Citrate-Dithionite Extraction

1. Weigh approximately 4.00 g air-dry mineral or organic soil into a 250-mL centrifuge bottle and record exact weight [30-B] and [31-B]. Add 125 mL of the citrate-dithionite extraction solution, cap, and shake overnight (16 hours) on a reciprocating box shaker at 1 to 2 cycles per second.

2. Add 4 mL of 0.2 percent Superfloc solution and shake vigorously for approximately 30 seconds. Centrifuge for 10 minutes (higher speeds and longer times may be required for soils high in silt and clay). Record total volume, 129 mL, used in the extraction [30-C] and [31-C].

3. Remove centrifuge bottle from centrifuge. Examine the supernatant for suspended clays. If the supernatant is not clear, repeat Step 2.

4. Decant and save the supernatant for Fe^{3+} and Al^{3+} analysis. Store the supernatant at 4 °C.

5. Analyze for Fe^{3+} and Al^{3+} by ICP.

6. Dilute any sample with concentration above the linear dynamic calibration range of the instrument.

7. Log aliquot volume, diluted volume, and measured concentration as follows: Fe^{3+}: [30-D], [30-E], [30-F]; Al^{3+}: [31-D], [31-E], [31-F].

16.7 Calculations

NOTE: Designations within the square brackets, [ ], represent the form number and column in which the data are entered on forms 25, 26, 27, 28, 29, 30, 31, and 1 (Appendix B, figures B-61, B-62, B-63, B-64, B-65, B-66, B-67, and B-9).

$$\text{Cation (wt\%)} = \{[\text{inst. reading}] \times ([\text{diluted vol.}] \div [\text{aliq. vol.}]) \times [\text{initial extract vol.}] \times 1000\ \text{mL} \times 1\ \text{g mg} \times 100 \times 1\} \div \{[\text{sample wt.}] \times (1 - [\text{Moist}]) \div (100 + [\text{Moist}])\}$$

Pyrophosphate Extract:

$$\text{FE\_PYP [25-G]} = \{[\text{25-F}] \times ([\text{25-E}] \div [\text{25-D}]) \times [\text{25-C}] \times 0.0001 \times 1\} \div \{[\text{25-B}] \times (1 - [\text{1-D}]) \div (100 + [\text{1-D}])\}$$

$$\text{AL\_PYP [26-G]} = \{[\text{26-F}] \times ([\text{26-E}] \div [\text{26-D}]) \times [\text{26-C}] \times 0.0001 \times 1\} \div \{[\text{26-B}] \times (1 - [\text{1-D}]) \div (100 + [\text{1-D}])\}$$

Acid-Oxalate Extract:

$$\text{FE\_AO [27-G]} = \{[\text{27-F}] \times ([\text{27-E}] \div [\text{27-D}]) \times [\text{27-C}] \times 0.0001 \times 1\} \div \{[\text{27-B}] \times (1 - [\text{1-D}]) \div (100 + [\text{1-D}])\}$$

$$\text{AI\_AO [28-G]} = \{[\text{28-F}] \times ([\text{28-E}] \div [\text{28-D}]) \times [\text{28-C}] \times 0.0001 \times 1\} \div \{[\text{28-B}] \times (1 - [\text{1-D}]) \div (100 + [\text{1-D}])\}$$

$$\text{SI\_AO [29-G]} = \{[\text{29-F}] \times ([\text{29-E}] \div [\text{29-D}]) \times [\text{29-C}] \times 0.0001 \times 1\} \div \{[\text{29-B}] \times (1 - [\text{1-D}]) \div (100 + [\text{1-D}])\}$$

Citrate Dithionite Extract: FE_CD [30-G] = $\{[30\text{-}F] \times ([30\text{-}E] + [30\text{-}D]) \times [30\text{-}C] \times 0.0001 \times 1\} + \{[30\text{-}B] \times (1 - [1\text{-}D]) + (100 + [1\text{-}D])\}$

AL_CD [31-G] = $\{[31\text{-}F] \times ([31\text{-}E] + [31\text{-}D]) \times [31\text{-}C] \times 0.0001 \times 1\} + \{[31\text{-}B] \times (1 - [1\text{-}D]) + (100 + [1\text{-}D])\}$

16.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water*, D-1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Fassel, V. A. 1982. *Analytical Spectroscopy with Inductively Coupled Plasmas - Present Status and Future Prospects.* In: Recent Advances in Analytical Spectroscopy Pergamon Press, New York, New York.

Fernandez, I. 1983. *Field Study Program Elements to Assess the Sensitivity of Soils to Acidic Deposition Induced Alterations in Forest Productivity.* Technical Bulletin No. 404. National Council of the Paper Industry for Air and Stream Improvement, Inc. New York, New York.

Johnson, D. W. and D. E. Todd. 1983. Some Relationships among Fe, Al, C, and SO_4 in a Variety of Forest Soils. *Soil Sci. Soc. Am. J.*, 47:702 -800.

U.S. Environmental Protection Agency. 1983 (revised). *Methods for Chemical Analysis of Water and Wastes. Method 200.0, Atomic Absorption Methods and Method 200.7, Inductively Coupled Plasma Atomic Emission Spectrometric Method for the Trace Element Analysis of Water and Wastes.* EPA/600/4-79/020. U.S. Environmental Protection Agency, Cincinnati, Ohio.

17.0 Extractable Sulfate

17.1 Overview

Sulfur, in the form of sulfate (SO_4^{2-}) is the principal anion in acidic deposition in the eastern U.S. The ability of soils to adsorb sulfate is one of the principal factors affecting the rate and extent of soil and watershed response to acidic deposition. Quantification of existing pools of adsorbed sulfate on a soil, concurrent with measurements of sulfate adsorption capacity of that soil, provide useful information for understanding the status and for predicting the future response of the soil to acidic deposition.

Sulfate can be adsorbed to soil in several ways, which in turn affect the extent to which that sulfate can be displaced or exchanged from the soil surface. Sulfate held by electrostatic bonding is weakly held and can be readily exchanged by other anions. In addition sulfate can be adsorbed by exchange of one or a pair of ligands (covalent bonds between an oxyanion and metal oxides on the soil surface). Two extractions have been developed to characterize the amount of sulfate present on the soil and extent to which it is reversibly sorbed. Water extraction (deionized water) removes free sulfate salts in the soil (usually present in negligible amounts), sulfate retained on the soil by electrostatic bonding, and a portion of sulfate retained by ligand exchange; the extent to which the latter is removed is highly variable and is dependent on the solid-solution phase partitioning characteristics of the soil. Phosphate (PO_4^{3-}) extraction, in contrast, is intended to provide a quantitative extraction of adsorbed sulfate. Phosphate forms stronger ligands with metal oxide surfaces than does sulfate and is thus preferentially adsorbed, displacing sulfate from adsorption sites. The relative ligand strengths, along with mass action effects and sequential extractions in the phosphate technique, should provide nearly quantitative displacement of non-crystalline, inorganic sulfate from soil surfaces.

17.1.1 Summary of Method

Two aliquots of a soil sample are extracted. Deionized (DI) water is the extracting matrix for readily available sulfate. The extracting matrix for sulfate that is more difficult to dislocate is 0.016 M sodium phosphate (containing 500 mg P/L). After the extractions are completed, the analytes are determined by ion chromatography (IC).

17.1.2 Interferences

An interference can occur during the ion chromatographic analysis of the 0.016 M NaH_2PO_4 extract. At such a high concentration, the phosphate peak overlaps the SO_4^{2-} peak under typical IC conditions (usually phosphate elutes prior to sulfate). By using the mixed eluent 0.0020 M Na_2CO_3/0.0020 M NaOH (an eluent whose pH is greater than the pK of HPO_4^{2-} [pK = 12.37] and which is sufficiently buffered to maintain the pH in the presence of the eluting phosphate), phosphate elutes after SO_4^{2-}, and the interference is minimized or eliminated. Elution time for sulfate is increased by nearly ten minutes with this modification.

Soil extracts can rapidly degrade a column; therefore, cleaning with dilute acid is recommended after every 50 samples. Also, the use of guard columns is highly recommended to extend the life of the separator column and improve analytical reproducibility.

17.1.3 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. Follow the safety precautions of the manufacturer when operating instruments.

17.2 Sample Collection, Preservation, and Storage

A subsample is taken from the bulk soil sample after it has been air dried, homogenized, and tested for moisture content (see sections 4.0 and 8.0). Samples should be stored at 4 °C until ready for analysis. Preparation of the soil extractions is described in sections 17.6.1 and 17.6.2.

17.3 Equipment and Supplies

17.3.1 Equipment Specifications

1. Ion chromatograph, Dionex models 10, 12, 14, 16, or 2000 series or equivalent with AS3, AS4a, or equivalent anion separator column, anion fiber or micromembrane suppressor column or equivalent; appropriate guard column is required to preserve the separator column.

2. Automated injection system, commercially available from several manufacturers.

3. Data recording system, integrator or strip chart recorder for recording ion chromatographs; the nominal output to recorder is 1.0 volts. The Dionex plane parallel electrode conductivity detector or equivalent unit gives a linear response with concentration until electronic saturation occurs at approximately 4.0 volts. Therefore, several analytical ranges on recorders set at different full-scale voltages can be monitored simultaneously.

17.3.2 Apparatus

1. Balance, capable of weighing to 0.001 g.

2. Centrifuge.

3. Filtration apparatus.

4. Reciprocating shaker.

5. Vortex mixer (optional).

6. Volumetric pipets, volumes as needed.

7. Volumetric flasks, volumes as needed.

8. Balance calibration weights, 3-5 weights covering expected range.

17.3.3 Reagents

Unless stated otherwise, all chemicals must be American Chemical Society (ACS) Reagent Grade or better. The concentrated and working eluents, as well as the regenerant used, are based on the recommendation of the manufacturer for the particular column and instrument used. These may be altered to increase resolution or decrease separation time. The eluents, suppressors, and regenerants are presented for a Dionex unit with an AS series anion separator column. These will change with the manufacturer and column used. All modifications should be documented before routine analysis begins.

1. Phosphate extract solution ($NaH_2PO_4 \cdot H_2O$), 0.016 M (500 mg P/L)--For extraction of routine soils; dissolve 22.27 g $NaH_2PO_4 \cdot H_2O$ in DI water and dilute to 10.00 L.
2. Phosphate standard solution ($NaH_2PO_4 \cdot H_2O$), 0.032 M (1,000 mg P/L)--For standards; 4.454 g $NaH_2PO_4 \cdot H_2O$ in DI water and dilute to 1.00 L.
3. Concentrated eluent, 0.40 M Na_2CO_3--Dissolve 42.40 g Na_2CO_3 in DI water and dilute to 1.00 L. Seal and store until use.
4. Sodium hydroxide (50 percent wt/v)--Dissolve 50 g NaOH (pellets or flakes) in DI water and dilute to 100 mL. This dissolution generates heat; therefore, a water or ice-bath should be used to cool the dissolution vessel. Alternately, allow solution to stand overnight to cool. Sodium carbonate may precipitate.
5. Working eluent, 0.0020 M Na_2CO_3/0.0020 M NaOH--Dilute 20.0 mL concentrated eluent to 4.00 L and adjust pH to 12.5 with 50 percent NaOH. Other working eluents for the IC type columns include: (1) 0.003 M Na_2CO_3 for water extractable sulfate and 0.002 M $NaHCO_3$/0.0025 M NaOH for phosphate extractable sulfate, and (2) 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 for both sulfates. The eluent used must give clean separation of the peaks without excessive band broadening.
6. Sulfuric acid (H_2SO_4), 2.5 M--Dilute 34.7 mL concentrated H_2SO_4 to 1.00 L.
7. Fiber suppressor regenerant--For water-extractable samples, H_2SO_4 (0.025 M)--Dilute 10 mL of 2.5 M H_2SO_4 to 1.0 L with DI water. This can be made in large batches and stored for later use (up to one year).
8. Magnesium sulfate ($MgSO_4$), anhydrous--Must be dried and desiccated prior to weighing.
9. Stock standard (1,000 mg S/L)--Dissolve 3.75 g $MgSO_4$ in DI water and dilute to 1.00 L.
10. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

17.3.4 Consumable Materials

1. Centrifuge tubes, with screw caps (50-mL centrifuge tubes with screw caps, optional).
2. Membrane filters, 0.45-µm pore; rinsed three times with DI water.

3. Parafilm.
4. Weighing pans, disposable.
5. Forms--Form 32, water extractable sulfate, Form 33, phosphate extractable sulfate, Form QC-32, Form QC-33, and IC Form (Appendix B, figures B-75 through B-79, respectively).

17.4 Calibration and Standardization

17.4.1 Water Extract

Dilute aliquots of the stock standard (Section 17.3.3, Step 9) with DI water to prepare five calibration standards ranging from 0 to 5 mg S/L. These calibration standards should be prepared fresh daily. Other concentrations may be used as long as the calibration standards bracket the sample concentrations. Follow the procedure given in Section 17.6.3.2.

17.4.2 Phosphate Extract

Add 25.0 mL of the phosphate standard solution to 50.0 mL volumetric flasks and aliquots of the stock standard (Section 17.3.3, Step 9) to prepare five calibration standards ranging from 0 to 10 mg S/L when the mixture is diluted to 50.0 mL with DI water. This results in a series of calibration standards of 0-10 (mg S/L) in 500 mg P/L. These standards should be prepared fresh daily. Other concentrations of sulfate (mg S/L) may be used as long as the calibration standards bracket the sample concentrations. Follow the procedure given in Section 17.6.3.2.

17.5 Quality Control

Log the quality control (QC) data on forms QC-32 and QC-33 (Appendix B, figures B-77 and B-78); refer to Section 3.0 for additional information concerning these internal quality control checks. Record IC resolution test data on Form IC (Appendix B, Figure B-79).

Calibration Blanks--Calibration blanks (0.00 mg S/L standard) should be analyzed before the initial sample analysis, at specified intervals thereafter (e.g., after every ten samples) and after the last sample of each batch. Measured results for each blank should be 0.025 mg S/L or less. If the blank is higher than this limit, check the system and reanalyze all samples since the last acceptable calibration blank.

Reagent Blanks--Three reagent blanks, carried through the extraction procedure, are analyzed with each batch of samples. The calculated concentration of each blank should be less than or equal to the contract-required detection limit (CRDL) listed in Table 3-2.

Replicates--One sample from each batch should be weighed, extracted, and analyzed in duplicate for each of the two extractable sulfate extracts. The percent relative standard deviation (%RSD) should meet the limits outlined in Table 3-3.

QC Standards--These standards should be prepared from standards having the same composition as the stock standard but from a separate source of sulfate. One detection limit quality control check standard (DL-QCCS) having a known concentration of about 0.10 mg S/L in each extract should be analyzed with each batch of samples. Measured values should be within 20 percent of the known value.

QCCSs of concentrations at about mid-calibration range of the samples being analyzed should be measured before the first sample, at specified intervals thereafter (e.g., every tenth sample) and after the last sample of each batch of samples for both extracts. Measured values for each QCCS should be within 10 percent of the known value.

Matrix Spikes--For each batch of soils, one sample is spiked with a known concentration of sulfate. The concentration of sample plus spike should be between 1.5 and 3 times the measured concentration of the sample with no spike. In determining the recovery of the spike, the volume of the spike is assumed to be negligible. Recovery should be 90 to 110 percent of the spike concentration.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy windows provided by the quality assurance (QA) manager.

IC Resolution Test--When using an ion chromatograph, an IC resolution test should be performed before each day's analyses. One test should be made with each chromatograph used in these analyses. Resolutions are calculated for sulfate-phosphate and sulfate-nitrate. Data from each IC resolution test are reported on Form IC (Appendix B, Figure B-79; see also Section 3.2.7). Resolutions should be 60 percent or greater. If the resolution does not meet this criterion, no samples should be analyzed until corrective action is taken to provide acceptable resolution.

17.6 Procedure

Before proceeding with the analytical procedure, the analyst should be certain that all QC procedures have been implemented, all labware has been properly cleaned, and valid instrumental detection limits (IDLs) have been obtained, as outlined in Section 3.0 and Appendix A. Data should be logged following the procedures described in Section 3.0.

NOTE: Figures within the square brackets, [ ], represent the form number and column in which the data are entered.

17.6.1 Extraction of Sulfate by Deionized Water

1. Weigh 4.00 g air-dry mineral soil or 2.00 g air-dry organic soil into a 100-mL centrifuge tube. Add 80.0 mL DI water and seal the tube. If a 50-mL centrifuge tube is used, weigh 2.00 g mineral soil or 1.00 g organic soil and add 40.0 mL DI water. Record weight [32-B] and initial volume [32-C].
2. Shake tube and contents for 1 hour on a reciprocating box shaker at 1 to 2 cycles per second. To ensure that soil is not accumulating at the base of each centrifuge tube, stop the shaker at 10 to 15 minute intervals and either invert each tube several times by hand or mix each tube on a vortex mixer.
3. Centrifuge for 10 minutes. If the supernatant is not clear, repeat centrifugation. When it is clear, decant and save the supernatant.
4. Filter the supernatant solution through a 0.45-μm membrane filter.
5. Store the solution at 4 °C and analyze for sulfate by ion chromatography within 24 hours (see Section 17.6.3).

17.6.2 Extraction of Sulfate by Sodium Phosphate (NaH_2PO_4) Solution

1. Place 5.00 g of air-dry mineral soil or 2.50 g of air-dry organic soil into a 100-mL centrifuge tube. If 50-ml centrifuge tubes are used, weigh 2.50 g of air-dry mineral soil or 1.25 g air-dry organic soil.
2. Add 20 mL 0.016 M NaH_2PO_4 (500 mg P/L), or 10 mL if 50-mL centrifuge tubes are used.
3. Shake tube on a reciprocating box shaker for 30 minutes at 1 to 2 cycles per second. To ensure that soil is not accumulating at the base of each centrifuge tube, stop the shaker after 10 minutes and either invert each tube several times by hand or mix each tube on a vortex mixer.
4. Centrifuge for 10 minutes. If the supernatant is not clear, repeat centrifugation. When it is clear, decant supernatant into a clean, 100-mL volumetric flask.
5. Repeat steps 2, 3, and 4 three times. Combine all 4 supernatants and bring to 100.00-mL volume with phosphate extraction solution (500 mg/L P/L). Log sample weight [33-B] and final volume [33-C], 100.0 mL (or 50 mL if 2.50 g sample of a mineral soil or 1.25 g of an organic soil is used).
6. Filter the diluted extract solution through a 0.45-µm membrane filter.
7. Store the solution at 4 °C and analyze for sulfate by ion chromatography within 24 hours (see Section 17.6.3).

17.6.3 Determination of Sulfate by Ion Chromatography

This procedure is based on methods employing Dionex ion chromatographs. Other equivalent systems may be used with modifications to the columns, chromatographic conditions, and reagents. In these cases, follow the recommendations of the manufacturer. Analyze both the water and phosphate extracts of the soil samples.

17.6.3.1 Operating Specifications--

The following operating specifications and procedures are recommended for the Dionex-type system. Other systems require similar procedures.

- Recording system, 10 or 30 µS/cm full scale deflection; 100 µS/cm for some cases; linearity should be checked regularly since this may vary and cause error.
- Injection loop, 0.05 or 0.10 mL; 50 µL may be preferable for some phosphate samples to reduce pH problems.
- Flow rate, 2.0 to 2.3 mL/min.

- Pressure gauge or similar device, used as pump-stroke noise suppressor, as required for unit.

  NOTE: Make certain that pressure does not exceed the recommendations of the manufacturer for the column.

17.6.3.2 Procedure--

1. Operate the fiber or micromembrane suppressor as recommended by the manufacturer. Generally, the suppressor must be in an upright position with regenerant flowing from bottom to top.

2. Set up the recorders or integrators for the most sensitive setting for the sample range being analyzed. Set the second channel for a high range, or perform dilutions when necessary. Operate integrators according to the instructions of the manufacturer.

3. Pump eluent through the columns. After a stable baseline is obtained, adjust the recorder zero to approximately 10 percent of the chart. Inject the highest standard. As the highest standard elutes, adjust the recorder range to approximately 90 percent of the chart. Repeat several analyses of the highest standard to be certain that the gain is stable and the peaks are reproducible. Analyze the resolution standard and determine the resolution. If the phosphate-sulfate resolution does not exceed 60 percent, replace or clean the separator column and repeat from Step 1.

4. Analyze the standards in random order. Load the injection loop, manually or via the autosampler, with the standard to be analyzed. Load five to ten times the volume required to flush the sample loop thoroughly; then inject the standard. Wash injector loop thoroughly between each sample. For each analysis, measure and record the peak height either manually or with a data system. If an integrator is available, record the peak area.

5. Repeat Step 4 for analysis of QC samples, matrix spikes, blanks, and soil extracts. If using an autosampler, fill it with the samples.

6. Dilute and reanalyze each sample for which the concentration exceeds the calibrated range. Log in data as follows: water extract: aliquot volume [32-D], diluted volume [32-E], concentration (instrument reading in mg S/L) [32-F]; phosphate extract: aliquot volume [33-D], diluted volume [33-E], concentration (instrument reading in mg S/L) [33-F].

   NOTE: Use 0.16 M phosphate extract solution (17.3.3, Step 1) for phosphate extracts.

17.7 Calculations

NOTE: Designations within the square brackets [ ] represent the form number and column in which the data are entered on forms 32, 33, and 1 (Appendix B, figures B-75, B-76, and B-9).

Built-in microprocessors, available with many instruments, provide the most valid results. The use of these read-outs should be approved by the laboratory or QA manager; otherwise, one of the alternative techniques should be used:

From the peak heights, calculate the analyte concentration in the extract as follows:

1. Use a graph--Construct a calibration curve by plotting concentration of standard versus peak height (or peak area) for each standard. Read the concentration of the analyte directly from the calibration curve.

2. Use a linear least squares fit.

Extractable Sulfate (mg S/kg) = {[Inst. reading] × ([dilut. vol.] + [aliq. vol.]) × [Init. extract vol.] × (1 L/1000 mL) × (1000 g / kg) × 1} + {[sample wt.] × (1 - [MOIST]) + (100 + [MOIST])}

SO4_H2O [32-G] = {[32-F] × ([32-E] + [32-D]) × [32-C] × 1} + {[32-B] × (1 − [1-D]) + (100 + [1-D])}

SO4_PO4 [33-G] = {[33-F] × ([33-E] + [33-D]) × [33-C] × 1} + {[33-B] × (1 − [1-D]) + (100 + [1-D])}

17.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards Vol. 11.01, Standard Specification for Reagent Water*, D-1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

18.0 Sulfate Adsorption Isotherms

18.1 Overview

The ability of a soil to adsorb sulfate (SO_4^{2-}) is one of the principal factors affecting the rate and extent of soil response to acidic deposition. Sulfate adsorption by a soil will result in a proportional delay or reduction in cation leaching from the soil, and in soils with high adsorption capacity can delay the onset of adverse effects on surface waters for several decades. Sulfate (or other anion) adsorption capacity is related to several other soil variables; adsorption increases with surface area and Fe^{2+}/Al^{3+} hydrous oxide content in the soil, varies inversely with soil pH (Tabatabai, 1982) and inversely with soil organic content. The ability of a soil to adsorb SO_4^{2-} can be characterized by development of an adsorption isotherm (i.e., a partitioning function relating relationships between concentrations of dissolved and adsorbed SO_4^{2-} over a useful concentration range). The procedures described here provide data used to generate such an isotherm for soils, but do not describe actual generation of an isotherm. Procedures described here measure net SO_4^{2-} retention by soils for a range of SO_4^{2-} adsorption corresponding to the equilibrated concentration of dissolved SO_4^{2-} for each slurry, and an isotherm can then be fitted by regression to the resulting set of data points for each individual soil. (Fernandez, 1983; Johnson and Todd, 1983.)

18.1.1 Scope and Application

Sulfate adsorption isotherms are analyzed only for mineral soils (see Section 7.7 for determination of mineral and organic soils).

The most direct and effective way to determine sulfate-adsorption capacity utilizes sulfate adsorption isotherms. In this method, sulfate adsorption isotherms are developed by measuring the amount of sulfate remaining in solution after contact with a soil sample. These sulfate adsorption isotherms allow comparisons to be made between horizons or between pedons.

18.1.2 Summary of Method

Six aliquots of the same soil sample are shaken with solution containing 0, 2, 4, 8, 16, and 32 mg sulfur per liter, respectively. The mixtures are centrifuged and filtered, and the resulting filtrate is analyzed for sulfate by ion chromatography (IC). The difference between the original concentrations of the sulfur solutions and the final concentrations after this procedure indicates the sulfur uptake or release by the soil.

18.1.3 Interferences

Soil texture, iron and aluminum content, pH, and organic content of the soil are factors which affect adsorption capacity; alteration of these properties by sample processing should be avoided. Calcium, magnesium, or potassium salts may be used; use of sodium salts is not recommended.

18.1.4 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids should be restricted to a fume hood. Follow the safety precautions of the manufacturer when operating the instruments.

18.2 Sample Collection, Preservation, and Storage

A subsample is taken from the bulk soil sample after it has been air dried, homogenized, and tested for moisture content (see sections 4.0 and 8.0). Samples should be stored at 4 °C until ready for analysis. Sample preparation is described in Section 18.6.1.

18.3 Equipment and Supplies

18.3.1 Equipment Specifications

1. Ion chromatograph, Dionex models 10, 12, 14, 16, or 2000 series or equivalent with AS3, AS4a, or equivalent anion separator column, anion fiber or micromembrane suppressor column or equivalent; appropriate guard column is required to preserve the separator column.

2. Automated injection system, commercially available from several manufacturers.

3. Data recording system, integrator or strip chart recorder for recording ion chromatographs; the nominal output to recorder is 1.0 volts. The Dionex plane parallel electrode conductivity detector or equivalent unit gives a linear response with concentration until electronic saturation occurs at approximately 4.0 volts. Therefore, several analytical ranges on recorders set at different full-scale voltages can be monitored simultaneously.

18.3.2 Apparatus

1. Balance, capable of weighing to 0.01 g.

2. Volumetric pipet, 50-mL (pipettor, optional).

3. Vortex mixer.

4. Reciprocating shaker.

5. Centrifuge.

6. Membrane filtration apparatus (Luer-Lok, plastic or glass syringes with membrane filters or equivalent).

7. Balance calibration weights, 3-5 weights covering expected range.

18.3.3 Reagents and Consumable Materials

1. Primary sulfate SO_4^{2-} solution (1,000 mg S/L)--Dissolve 3.75 g anhydrous $MgSO_4$ in deionized (DI) water and dilute to 1.00 L. $MgSO_4$ must be dried and desiccated before weighing for sample preparation.

2. Adsorption solutions--Dilute 2.00, 4.00, 8.00, 16.00, and 32.00 mL of 1,000 mg S/L primary solution to 1.00 L in separate volumetric flasks. This yields working standards of 2.00, 4.00, 8.00, 16.00, and 32.00 mg S/L, respectively. It is most convenient if 2- to 4-L batches of adsorption solution can be prepared. Each solution must be within 3 percent of its theoretical concentration (2 percent for the 32.00 mg S/L primary solution).

3. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

4. Centrifuge tubes, 100-mL, with screw caps (50-mL centrifuge tubes with screw caps, optional).

5. Membrane filters, 0.45-μm pore size; washed three times with 100 mL of DI water.

6. Weighting pans, disposable.

7. Forms--Form 34, 0 mg S/L isotherm, Form 35, 2 mg S/L isotherm, Form 36, 4 mg S/L isotherm, Form 37, 8 mg S/L isotherm, Form 38, 16 mg S/L isotherm, Form 39, 32 mg S/L isotherm, forms QC-34 through QC-39, and Form IC (Appendix B, figures B-80 through B-91, and Figure B-79 respectively).

18.4 Calibration and Standardization

Calibrate the ion chromatograph as recommended by the manufacturer. Prepare working standards fresh daily and verify the concentrations by IC. Analyze adsorption solutions and report on forms QC-34 through QC-39 (Appendix B, figures B-86 through B-91, respectively). Log IC resolution test data on Form IC (Appendix B, Figure B-79). Remake adsorption solutions if the concentrations are not within 3 percent of the theoretical concentrations (2 percent for the 32 mg S/L solution). Calibration standards must be from a source independent of the primary sulfate solution prepared for this analysis.

18.5 Quality Control

Log the quality control (QC) data on forms QC-34 through QC-39 (Appendix B, figures B-86 through B-89); refer to Section 3.0 for additional information concerning these internal quality control checks.

Calibration Blanks--Calibration blanks (0.00 mg S/L standard) should be analyzed before the initial sample analysis, at specified intervals thereafter (e.g., after every ten samples) and after the last sample of each batch. Measured results for each blank should be 0.025 mg S/L or less. If any blank is higher than this limit, check the system and reanalyze all samples since the last acceptable calibration blank.

Reagent Blanks--Three reagent blanks are analyzed with each batch of samples. These blanks consist of the adsorption solutions (0 - DI water, 2, 4, 8, 16, and 32 mg S/L) passed through the analytical procedure without any soil being present. The reagent blanks should fall between: 1.94 to 2.06 for SO4_2, 3.88 to 4.12 for SO4_4, 7.76 to 8.24 for SO4_8, 15.52 to 16.48 for SO4_16, and 31.36 to 32.64 for SO4_32. The reagent blank should be 0.025 mg S/L or less for SO4 0.

Replicates--One sample from each batch should be weighed, extracted, and analyzed in duplicate for extracted sulfate calculated as mg S/L. The percent relative standard deviation (%RSD) should meet the limits listed in Table 3-3.

QC Standards--These standards should be prepared from standards having the same composition as the stock standard but from a separate source of sulfate. One detection limit quality control check standard (DL-QCCS) having a known concentration of about 0.3 mg S/L should be analyzed with each batch of samples. Measured values should be within 20 percent of the known value.

QCCSs of concentrations at about mid-calibration range of the samples being analyzed should be measured before the first sample, at specified intervals thereafter (e.g., every tenth sample) and after the last sample of each batch of samples for both extracts. Measured values for each QCCS should be within 5 percent of the known concentration.

Spike Solution--For each batch of samples, a spike solution should be analyzed in triplicate for S content. The spike solution consists of the adsorption solutions (0 - DI water, 2, 4, 8, 16, and 32 mg S/L) associated with the appropriate analytical test being performed. Measured values for the spike solution should be: ± the contract required detection limit (CRDL); 0.025 mg S/L for SO4_0; ± 3 percent of the known value for SO4_2, SO4_4, SO4_8, and SO4_16; and ± 2 percent of the known value for SO4_32.

Matrix Spikes--For each batch of soils, the 2-, 8-, and 32-mg S/L isotherms from two samples are spiked with known concentrations of sulfate. The concentration of sample plus spike should be between 1.5 and 3 times the measured concentration of the sample with no spike. In determining the recovery of the spike, the volume of the spike is assumed to be negligible. Recovery should be 95 to 105 percent of the spike concentration.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy windows provided by the quality assurance (QA) manager.

IC Resolution Test--When using an ion chromatograph, an IC resolution test should be performed before each sample analysis run. One test should be made with each chromatograph used in these analyses. Resolutions are determined for sulfate-phosphate and sulfate-nitrate. Data from each IC Resolution Test are reported on Form IC (Appendix B, Figure B-79; see also Section 3.2.7). Resolutions should be 60 percent or greater. If the resolution does not meet this criterion, no samples should be analyzed until corrective action is taken to provide acceptable resolution.

18.6 Procedure

Before proceeding with the analytical procedure, the analyst should be certain that all QC procedures have been implemented, all labware has been properly cleaned, and valid instrumental detection limits (IDLs) have been obtained, as outlined in Section 3.0 and Appendix A. Data should be logged following the procedures described in Section 3.0.

NOTE: Figures within the square brackets, [ ], represent the form number and column in which the data are entered.

18.6.1 Sample Preparation

1. Weigh 10.00 g air-dry sample to the nearest 0.01 g and place in a 100-mL centrifuge tube. Log exact weight [34-B].

   NOTE: If a 50-mL centrifuge tube is used, reduce sample weight to 5.00 g air-dry mineral soil.

2. Add 50.0 mL of DI water to centrifuge tube and cap the tube. Mix contents with vortex mixer until no soil adheres to the bottom of the centrifuge tube. If a 50-mL centrifuge tube is used, reduce volume to 25.0 mL. Log [34-C].

3. Repeat steps 1 and 2 and substitute 2-, 4-, 8-, 16-, and 32-mg S/L solutions for DI water. Log weight and volume data for 2 mg S/L, [35-B] and [35-C]; 4 mg S/L, [36-B] and [36-C]; 8 mg S/L, [37-B] and [37-C]; 16 mg S/L, [38-B] and [38-C]; 32 mg S/L, [39-B] and [39-C].

4. Shake the samples for 1 hour on a reciprocating shaker at a rate sufficient to maintain the soil in suspension.

5. Centrifuge each sample until supernatant is clear.

6. Filter supernatant through a pre-rinsed 0.45-μm membrane filter.

7. Analyze solutions for sulfate by ion chromatography as described below.

18.6.2 Determination of Sulfate by Ion Chromatography

This procedure is based on methods employing Dionex ion chromatographs. Other equivalent systems may be used with modifications to the columns, chromatographic conditions, and reagents. In these cases, follow the recommendations of the manufacturer. Analyze both the water and phosphate extracts of the soil samples.

18.6.2.1 Operating Specifications--

The following operating specifications and procedures are recommended for the Dionex-type system. Other systems require similar procedures.

- Recording system, 10 or 30 μS/cm full scale deflection; 100 μS/cm for some cases; linearity should be checked regularly since this may vary and cause error.

- Injection loop, 0.05 or 0.10 mL; 50 μL may be preferable for some phosphate samples to reduce pH problems.

- Flow rate, 2.0 to 2.3 mL/min.
- Pressure gauge or similar device, used as pump-stroke noise suppressor, as required for unit.

NOTE: Make certain that pressure does not exceed the recommendations of the manufacturer for the column.

18.6.2.2 Procedure--

1. Operate the fiber or micromembrane suppressor as recommended by the manufacturer. Generally, the suppressor must be in an upright position with regenerant flowing from bottom to top.

2. Set up the recorders or integrators for the most sensitive setting for the sample range being analyzed. Set the second channel for a high range, or perform dilutions when necessary. Operate integrators according to the instructions of the manufacturer.

3. Pump eluent through the columns. After a stable baseline is obtained, adjust the recorder zero to approximately 10 percent of the chart. Inject the highest standard. As the highest standard elutes, adjust the recorder range to approximately 90 percent of the chart. Repeat several analyses of the highest standard to be certain that the gain is stable and the peaks are reproducible. Analyze the resolution standard and determine the resolution. If the phosphate-sulfate resolution does not exceed 60 percent, replace or clean the separator column and repeat from Step 1.

4. Analyze the standards in random order. Load the injection loop, manually or via the autosampler, with the standard to be analyzed. Load five to ten times the volume required to flush the sample loop thoroughly; then inject the standard. Wash injector loop thoroughly between each sample. For each analysis, measure and record the peak height either manually or with a data system. If an integrator is available, record the peak area.

5. Repeat Step 4 for analysis of QC samples, matrix spikes, blanks, and soil extracts. If using an autosampler, fill it with the samples.

6. If any concentrations are above the range of the instrument, take an aliquot, dilute, reanalyze, and report as follows:

Isotherm	Aliquot Vol.	Diluted Vol.	Measured Conc.
0	[34-D]	[34-E]	[34-F]
2	[35-D]	[35-E]	[35-F]
4	[36-D]	[36-E]	[36-F]
8	[37-D]	[37-E]	[37-F]
16	[38-D]	[38-E]	[38-F]
32	[39-D]	[39-E]	[39-F]

18.7 Calculations

NOTE: Designations within the square brackets, [ ], represent the form number and column in which the data are entered on forms 34, 35, 36, 37, 38 and 39 (Appendix B, figures B-80, B-81, B-82, B-83, B-84, and B-85.

Concentration (mg S/L) = Instrument Reading × Diluted Volume ÷ Aliquot Volume

SO4_0 [34-G] = [34-F] × ([34-E] ÷ [34-D])

S04_2 [35-G] = [35-F] × ([35-E] ÷ [35-D])

SO4_4 [36-G] = [36-F] × ([36-E] ÷ [36-D])

SO4_8 [37-G] = [37-F] × ([37-E] ÷ [37-D])

SO4_16 [38-G] = [38-F] × ([38-E] ÷ [38-D])

SO4_32 [39-G] = [39-F] × ([39-E] ÷ [39-D])

18.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water,* D-1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Fernandez, I. 1983. *Field Study Program Elements to Assess the Sensitivity of Soils to Acidic Deposition Induced Alterations in Forest Productivity. Technical Bulletin No. 404.* National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York.

Johnson, D. W., and D. E. Todd. 1983. Some Relationships Among Iron, Aluminum, Carbon, and Sulfate in a Variety of Forest Soils. *Soil Sci. Soc. Amer. J.* 47:702-800.

Tabatabai, M. A. 1982. Sulfur, pp. 501-538 In: *Methods of Soil Analysis: Part 2, Chemical and Microbiological Properties.* Agronomy Monograph No. 9, 2nd Edition. A. L. Page, R. H. Miller, and D. R. Keeney (eds.), American Society of Agronomy/Soil Science Society of America, Madison, Wisconsin.

19.0 Total Carbon and Nitrogen

19.1 Overview

Carbon and nitrogen are major components of soil organic material; quantification of them provides information about the amount and nature of organic material in the soil. Characterization of organic C and N also provides insight about the potential for uptake or release of nitrogen and/or sulfur by the soil organic matter due to microbial activity. Organic content of a soil affects sulfate adsorption and cation exchange properties of the soil, and organic content is used for certain soil taxonomic classifications. Carbon and nitrogen can occur in soils as inorganic forms (carbonates, nitrate, and ammonium); methods for analyses of inorganic forms are not included here. Inorganic forms of C and N are assumed to represent a minor fraction of total C and N in soils potentially sensitive to acid deposition. Analyses of total carbon and nitrogen were conducted using automated elemental analyzers.

19.1.1 Summary of Method

After sample processing and analysis for moisture content (sections 4.0 and 8.0), a soil sample is oxidized at temperatures greater than 1,000 °C with catalysts as specified by the instrument manufacturer. The evolved gases (CO_2 and N_2) are determined by thermal conductivity or infrared (IR) spectroscopy.

19.1.2 Interferences

Although moisture can interfere with certain carbon-hydrogen-nitrogen (CHN) analyses by producing large responses for total H, this interference can be eliminated in elemental analyses with moisture traps. Drying can cause losses of volatile organic materials containing C and N, and decomposition and loss of certain carbonates and ammonium salts. The samples may be freeze-dried to minimize these losses if approved by the quality assurance (QA) manager. These analyses are made on air-dry soils and the results corrected to an oven-dry basis.

Ambient N_2 and CO_2 not associated with the sample present possible gaseous interferences. Care must be taken with the blank to hold N_2 and CO_2 below the contract required detection limit (CRDL). The use of high purity carrier gas or helium helps reduce CO_2.

Soil residue can accumulate at the top of the combustion column. The column should be cleaned if sufficient residue accumulates that analytical results are affected.

19.1.3 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids and hydroxide solutions should be restricted to a fume hood. Heat resistant gloves may be needed when placing samples in the furnace. The furnace must be adequately vented and protected from human contact and combustible materials. Gas cylinders should be bolted or chained in an upright position.

19.2 Sample Collection, Preservation, and Storage

A subsample is taken from the bulk soil sample after it has been air dried, homogenized, and tested for moisture content (see sections 4.0 and 8.0). Samples should be stored at 4 °C until ready for analysis.

NOTE: The subsample may be ground to pass a No. 60 (U.S. No.) or No. 100 seive, if desired.

19.3 Equipment and Supplies

19.3.1 Apparatus and Equipment

NOTE: This list is generic for C and N methods. The specific requirements will vary with the instrument and procedures used. Some additional apparatus may be required; other equipment may not be needed.

1. Analyzer for Total C and N, Carlo-Erba model 1500 or equivalent.
2. Balance, capable of weighing to ±0.001 mg (±1 µg).
3. Balance calibration weights, 3-5 weights covering expected range.

19.3.2 Reagents and Consumable Materials

1. Catalysts and combustion accelerators (as needed).
2. Oxygen with in-line filter (high purity).
3. Carrier gases with in-line filter (as needed).
4. Standard Reference Material (SRM) 1646 (National Bureau of Standards [NBS]-standard estuarine sediment; 1.84% C, 0.176% N). NBS lists, but does not certify, a 0.96 percent sulfur content for this sample (Seward, 1988). Three years of Total C and N data for this standard are documented by G. Cutter, Old Dominion University, Norfolk, Virginia (personal communication, August 1988).
5. Absorbents (as needed).
6. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).
7. Vials, crucibles, boats, or tin sample capsules.
8. Forms--Form 40 total carbon, Form 41 total nitrogen, Form QC-40, and Form QC-41 (Appendix B, figures B-92 through B-95, respectively).

19.4 Calibration and Standardization

Follow the instrument manufacturer's instructions regarding calibration and standardization. In general, the instrument should be calibrated at least once per day or once per batch of samples, whichever is more frequent. Use either NBS reference materials or standards supplied by the manufacturer and approved by the laboratory or QA manager. The concentration range of the standards must be representative of the C and N concentrations in the soil samples. Use a sample of SRM 1646 as an initial calibration check.

If the nitrogen peak tends to consistently increase it may indicate that oxygen gas is overshadowing the nitrogen peak. If this is the case, replace or regenerate the copper oxide scrubber.

Combustion accelerators may be necessary if incomplete combustion occurs. Use vanadium pentoxide or consult manufacturer's recommendations.

19.5 Quality Control

Log all QC data on Form QC-40 or QC-41 (Appendix B, figures B-94 and B-95, respectively); refer to Section 3.0 for additional details concerning the internal QC checks.

Calibration Blanks--Calibration blanks should be analyzed before the initial sample analysis, at specified intervals thereafter (e.g., after every ten samples) and after the last sample of each batch for both carbon and nitrogen. If the instrument does not produce a blank value in weight percentage, the value should be determined from the instrument readout (or blank used in calibration and standardization), the instrumental factor (relating read-out to weight, μg, of element), and an appropriately assumed sample size (the smallest acceptable weight given by the manufacturer of the instrument; in general, 0.1 mg). Each blank should be less than the CRDL listed in Table 3-2. If any blank is higher than this limit, check the system and reanalyze all samples since the last acceptable calibration blank.

Reagent Blanks--Three reagent blanks are analyzed with each batch of samples if catalysts or accelerators are used. Each blank should be less than the CRDL outlined in Table 3-2. No reagent blanks are necessary if catalysts or accelerators are not used.

Replicates--One sample from each batch should be analyzed in duplicate for total carbon and nitrogen. The percent relative standard deviation (%RSD) of the paired data should be 10 percent or less.

QC Standards--One detection limit quality control check standard (DL-QCCS) having a known concentration of about 0.03 weight percent for Total C and 0.015 weight percent for Total N should be analyzed with each batch of samples. Measured values should be within 20 percent of the known value.

Quality Control Check Standards (QCCSs) of concentrations at about mid-calibration range of the samples being analyzed should be measured before the first sample, at specified intervals thereafter (e.g., every tenth sample) and after the last sample of each batch of samples. Measured values of each QCCS should be within 10 percent of the known concentrations.

Matrix Spikes--For each batch of soils one sample is spiked with a standard containing known concentrations of carbon and nitrogen. The spike is weighed into the combustion capsule or boat before the sample is added. The concentration of sample plus spike should be between 1.5 and 3 times the measured concentration for each element in the sample with no spike. The amount of added spike is determined by multiplying the known concentration of the spike by the spike weight, divided by the weight of the sample being spiked. In determining the concentration of the sample plus spike, the weight of the spike is assumed to be negligible. Recovery should be 90 to 110 percent of the spike concentration.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy windows provided by the QA manager.

19.6 Analytical Procedures

Before proceeding with the analytical procedure, the analyst should be certain that all QC procedures have been implemented, all labware has been properly cleaned, and valid instrumental detection limits (IDLs) have been obtained, as outlined in Section 3.0 and Appendix A. Data should be logged following the procedures described in Section 3.0.

NOTE: Figures within the square brackets, [ ], represent the form number and column in which the data are entered.

1. Follow manufacturer's instructions to determine instrument factors and log in Total C, [40-C]; Total N, [41-C].
2. Weigh approximately 100 mg of air-dry mineral soil or 20 mg of organic soil and log exact weight for Total C [40-B]; and Total N, [41-B].
3. Perform analyses and blanks as recommended by instrument manufacturer and log the instrumental read-out for Total C, [40-D], [40-E]; and Total N, [41-D], [41-E]; in appropriate units.

   Note: Raw data on forms 40 and 41 (Appendix B, figures B-92 and B-93) are on an air-dry basis.

19.7 Calculations

NOTE: Designations within the square brackets, [ ], represent the form number and column in which the data are entered on forms 40, 41, and 1 (Appendix B, figures B-92, B-93, and B-9.

Element (Wt %) = {(([instrument reading] - [blank]) × [instrument factor] × 1} +
{[sample wt.] × (1 - [MOISTURE]) + (100 + [MOISTURE])) × 100

C_TOT [40-F] = {(([40-D] - [40-E]) x [40-C] × 1} + {[40-B] × (1 - [1-D]) + (100 + [1-D]))} × 100

N_TOT [41-F] = {(([41-D] - [41-E]) x [41-C] × 1} + {[41-B] × (1 - [1-D]) + (100 + [1-D]))} × 100

19.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water,* D-1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Seward, R. W. (ed.). 1988. *National Bureau of Standards Standard Reference Materials Catalog 1988-89.* NBS Special Publication 260, U.S. Government Printing Office, Washington, D.C.

20.0 Total Sulfur

20.1 Overview

The determination of total sulfur is useful for characterizing relationships between inputs of sulfur from acidic deposition and soil sulfur pools. In this method, total sulfur in soil samples is determined with an automated sulfur analyzer by combustion of the sample at approximately 1,370 °C. This procedure is based on the operating instructions for a LECO SC-132 sulfur analyzer (LECO Corporation, 1983), adapted to permit analysis of very low levels of total S (as low as 10 mg/L) in soils.

20.1.1 Summary of Method

The sample is placed in a ceramic crucible with combustion accelerators and heated to a maximum of 1,370 °C in a resistance furnace. The combustion of the sample liberates SO_2 which is determined by an infrared (IR) detector. A microprocessor calculates results by combining the outputs of the infrared detector and system ambient sensors with preprogrammed calibration, linearization, and mass compensation factors. This method is based on research by David et al. (1989).

20.1.2 Interferences

If the soil has a high organic matter content, sample size must be reduced to prevent an explosion in the furnace when heat and oxygen are added. Also, high organic matter content may delay combustion. Low recovery of sulfur may occur, since organic matter consumes oxygen to produce CO_2 and nitrogen oxides in addition to SO_2.

20.1.3 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids and hydroxide solutions should be restricted to a fume hood. Heat resistant gloves may be needed when placing samples in the furnace. The furnace must be adequately vented and protected from human contact and combustible materials. Gas cylinders should be bolted or chained in an upright position.

Fumes of magnesium oxide (MgO) are toxic. Magnesium perchlorate [$Mg(ClO_4)_2$] is a fire and explosion hazard if it comes in contact with organic materials.

20.2 Sample Collection, Preservation, and Storage

A subsample is taken from the bulk soil sample after it has been air dried, homogenized, and tested for moisture content (see sections 4.0 and 8.0). Samples should be stored at 4 °C until ready for analysis.

NOTE: The subsample may be ground to pass a No. 60 (U.S. No.) or No. 100 sieve, if desired.

20.3 Equipment and Supplies

20.3.1 Apparatus and Equipment

1. Sulfur analyzer, LECO model SC-132, or equivalent.
2. Sampling scoops (LECO or equivalent).
3. Balance, capable of weighing to ±0.01 mg.
4. Balance calibration weights, 3-5 weights covering expected range.

20.3.2 Reagents and Consumable Materials

1. Oxygen (high purity).
2. Anhydrous magnesium perchlorate [$Mg(ClO_4)_2$], 10-20 mesh, or equivalent desiccant specified by manufacturer for drying gases (after combustion and prior to detection).
3. Carrier gases (if needed).
4. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).
5. Combustion boats, sulfur-free and appropriate for use with the equipment used.
6. Forms--Form 42, Total sulfur and Form QC-42 (Appendix B, figures B-96 and B-97, respectively).

   NOTE: Certain instruments may not require the following materials. Refer to the instruction manual for the specific instrument and consult with the quality assurance (QA) manager.

7. Magnesium oxide (MgO), powder, American Chemical Society (ACS) reagent grade, low in sulfur.
8. V_2O_5, LECO Part No. 501-636.
9. LECO orchard leaves (0.169% S) for calibration.
10. National Bureau of Standards (NBS) Standard Reference Material (SRM) 1633a Coal Fly Ash (0.18% S).

20.4 Calibration and Standardization

Follow the procedure outlined in the operating manual of the specific instrument. Generally, the following steps are necessary:

1. Run up to five analyses to condition the instrument at the beginning of the day, whenever the instrument has been idle for a period of time, or whenever new desiccant has been installed.

2. Periodically, check the desiccant (magnesium perchlorate) in the drying tube and replace it whenever the first few centimeters become wet. If it becomes too wet, the baseline may shift as the sample starts to heat and this shift will be integrated with and computed as sulfur.

3. To prolong the life of the combustion tube and refractory liner, the furnace should remain at operating temperature at all times; however, to conserve energy the furnace temperature may be reduced slightly. Refer to the instrument manual for specific information.

The instrument should be calibrated once per day or once per batch, whichever is more frequent. Analyze a series of LECO orchard leaves (0.169% S) by the procedure given in the instruction manual for the specific instrument. Determine the weights of standard to use so that the analytical results for the standard bracket the expected sulfur content of the samples. Check calibration by running NBS sample SRM 1633a (0.18% S) before routine analysis.

Analyze no fewer than three standards that bracket the expected concentration range of the samples. When only one standard material is used for calibration, at least three samples of standard material of different weights are prepared such that: (1) the amount of sulfur produced by the smallest sample is approximately three to five times the instrument detection limit, (2) the amount of sulfur produced by the largest sample is above that of the actual samples, and (3) the amount of sulfur produced by the intermediate sample is in the mid-range of the analyte content of the samples. The values for these check samples should be within the contract specified limits.

20.5 Quality Control

Log all QC data on Form QC-42 (Appendix B, Figure B-97); refer to Section 3.0 for additional details concerning the internal QC checks.

Calibration Blanks--Calibration blanks should be analyzed before the initial sample analysis, at specified intervals thereafter (e.g., after every ten samples) and after the last sample of each batch. If the instrument does not produce a blank value in weight percentage, the value should be determined from the instrument readout (or blank used in calibration and standardization), the instrumental factor (relating read-out to weight, μg, of element), and an appropriately assumed sample size (the smallest acceptable weight given by the manufacturer of the instrument; in general 0.1 mg). Each blank should be less than the contract-required detection limit (CRDL) listed in Table 3-2. If any blank is higher than this limit, check the system and reanalyze all samples since the last acceptable calibration blank.

Reagent Blanks--Three reagent blanks, consisting of 1.0 g of V_2O_5, are analyzed with each batch of samples. Each blank should be less than the CRDL outlined in Table 3-2.

Replicates--One sample from each batch should be analyzed in duplicate. The percent relative standard deviation (%RSD) of the paired data should be 10 percent or less.

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QC Standards--One detection limit quality control check standard (DL-QCCS) having a known concentration of about 0.003 percent S should be analyzed with each batch of samples. Measured values should be within 20 percent of the known value.

QCCSs of concentrations at about mid-calibration range of the samples being analyzed should be measured before the first sample, at specified intervals thereafter (e.g., every tenth sample) and after the last sample of each batch of samples. Measured values of each QCCS should be within 10 percent of the known concentrations.

Matrix Spikes--For each batch of soils, one sample is spiked with a standard containing a known concentration of sulfur. The spike is weighed into the combustion capsule or boat before the sample is added. The concentration of sample plus spike should be between 1.5 and 3 times the measured concentration for each element in the sample with no spike. The amount of added spike is determined by multiplying the known concentration of the spike by the spike weight, divided by the weight of the sample being spiked. In determining the concentration of the sample plus spike, the weight of the spike is assumed to be negligible. Recovery should be 90 to 110 percent of the spike concentration.

QC Audit Sample (QCAS)--The QCAS should fall within the accuracy windows provided by the QA manager.

20.6 Analytical Procedure

Before proceeding with the analytical procedure, the analyst should be certain that all QC procedures have been implemented, all labware has been properly cleaned, and valid instrumental detection limits (IDLs) have been obtained, as outlined in Section 3.0 and Appendix A. Data should be logged following the procedures described in Section 3.0.

NOTE 1: Figures within the square brackets, [ ], represent the form number and column in which the data are entered.

NOTE 2: This method is based on David et al. (1989).

1. Weigh approximately 0.800 g of mineral soil (or 0.300 g of organic soil) into a new ceramic combustion boat using the integral balance (nearest 1 mg) and log exact weight in [42-B].
2. Add 1.00 g of V_2O_5 iron powder (LECO Part No. 501-636) to the boat. Mix the sample thoroughly with accelerators, taking care not to lose any sample material. Reproducible results for low concentration samples are dependent on thorough mixing.
3. Follow step-by-step analytical procedure as outlined in the instrument instruction manual.

20.7 Calculations

NOTE: Designations within the square brackets, [ ], represent the form number and column in which the data are entered on forms 42 and 1 (Appendix B, figures B-96 and B-9).

An instrument with internal calibration may report sulfur results in weight percent, although correction for moisture content of soil is still required.

$$\text{Sulfur (Wt \%)} = \{[\text{Instrument reading}] \times 1\} + \{[\text{sample wt.}] \times (1 - [\text{MOIST}]) + (100 + [\text{MOIST}]) \times 100\}$$

$$\text{S\_TOT [42-F]} = \{[\text{42-D}] \times 1\} + \{[\text{42-B}] \times (1 - [\text{1-D}]) + (100 + [\text{1-D}]) \times 100\}$$

Data from other instruments may require a series of calculations to express results as weight percent sulfur. Compare the sample results to a standard curve. Determine the sulfur content in mg, then convert to weight percent, as follows:

$$\text{\% Sulfur} = \text{mg S/g} \times 1000\ \text{mg/g} \times 100$$

$$\text{S\_TOT [42-F]} = \{[\text{42-D}] \times 0.1 \times 1\} + \{[\text{42-B}] \times (1 - [\text{1-D}]) + (100 + [\text{1-D}])\} \times 100$$

20.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water*, D-1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

David, M. B., M. J. Mitchell, D. Aldcorn, and R. B. Harrison. 1989. Analysis of Sulfur in Soil, Plant and Sediment Materials: Sample Handling and use of an Automate Analyzer. *Soil Biology and Biochemistry*. 21:119-123.

LECO Corporation. 1983. *Instruction Manual SC-132*. LECO Corporation, 300 Lakeview Ave., St. Joseph, Michigan 49085.

Appendix A

General Laboratory Procedures

Logbooks should be kept for each procedure or instrument. The logbook entries should include, at a minimum, all raw data, instrument and analyst identification, date and time of analysis, and comments on any unusual occurences or protocol deviations. The laboratory supervisor should review and sign the logbook at the completion of daily analyses. There should also be an instrument calibration logbook, including a record of the dates on which new chemicals are opened. Correct errors by writing a single line through the error and initialing the error. Always use ink when recording in the logbook.

NOTE: Gloves, lab coats, and safety glasses should be worn when contacting a sample, acids, or hazardous materials.

A.1 Cleaning Procedures for Labware

Clean all labware that comes into contact with the samples (e.g., sample bottles, centrifuge tubes, autosampler tubes, and cups) as described below.

A.1.1 Initial Cleaning

For new plastic ware, rinse each container with reagent grade methanol or ethanol. When cleaning plastic ware for reuse, the alcohol rinse may be omitted. Repeat this step if an oily residue appears during any analysis. Glassware does not need to be precleaned with alcohol.

A.1.2 Cleaning Reusable Labware

After an initial wash with tapwater, rinse each container three times with deionized (DI) water, three times with 3 N HCl (1:3 concentrated HCl:DI water), and three times with DI water as a final rinse.

After the initial cleaning, check 5 percent of the containers to ensure that rinsing has been adequate. Perform the check as follows:

> Add 500 mL of DI water to each clean, dry container or add the maximum volume if the capacity of the container holds less than 500 mL. Seal the container with a cap or with Parafilm, then rotate the container slowly until the water touches all surfaces. Allow the container to sit overnight. Remove the cap and measure the conductivity of the contained water. The conductivity must be less than 1 μS/cm. If any of the containers fail the check, rerinse all the containers and perform the check again on 5 percent of the rerinsed containers.

After the final rinse, empty the container, invert it, and allow it to dry. All plastic ware should be air-dried; glassware may be air-dried or oven-dried.

Place the plastic containers, capped or covered with Parafilm, in plastic bags which will remain sealed until the containers are used for sample analysis. Store glassware in a dust-free environment.

Syringes and centrifuge tubes may require the use of a brush and neutral pH detergent to remove adhering soil particles. A detergent wash must be followed by at least three tap-water rinses followed by three DI water rinses. Containers should be checked as described above.

Kjeldahl flasks should be cleaned with sulfuric acid because it is a good scavenger for ammonium ion.

Sedimentation cylinders may be cleaned by three deionized water rinses. The acid rinse may be omitted. Brushing may be required to remove adhering soil particles and, in extreme cases, a detergent wash followed by at least three tap-water rinses and three deionized-water rinses may be used.

A.2 Electronic Balance

A.2.1 Balance Standardization

Check standardization weekly and both prior to and after weighing chemicals used in preparing primary standards. Be sure to check the calibration over the entire range for which the balance is used.

1. While wearing gloves, use calibration weights ("S" class weights for analytical balances or "P" class weights for top-loading balances) to standardize the balance. Do not touch the weights with anything but forceps. Tare the balance and record the reading for each weight in the instrument calibration logbook.

2. If weight values and balance readings do not agree, consult the manufacturer's guide for adjustments.

A.2.2 Weighing Procedures

Always use a dry Teflon spatula. Do not use same spatula for successive weighings of different chemicals. Remember to weigh the substance with the lid on the balance if the balance had been originally tared with the lid on.

1. While wearing gloves, pour the approximate amount of substance needed into a weighboat. Do not put the spatula into the bottle.

2. Obtain a second weighboat, place it on the balance and tare.

3. Using a spatula, transfer the substance to the weighboat on the balance until the desired amount is obtained.

4. Dispose of any unused substance; do not return to bottle.

A.2.3 Cleanup

1. Rinse the spatula with deionized water after use and allow it to air dry.

2. Do not leave any spilled chemicals on the balance. Use a damp Kimwipe to clean the balance pan and wipe it dry.

A.3 Micropipet

The following instructions refer to the Finn continuous volume micropipets. These procedures can be modified for use with other digital micropipets. Keep pipet vertical at all times to prevent contamination.

A.3.1 Pipet Calibration

NOTE: Check the calibration of each pipet weekly, at a minimum, and record data in the instrument calibration logbook. Each procedure requires a daily calibration check of all pipets used. These data are recorded in the corresponding procedural logbook.

1. Calibrate pipets as follows, setting the volume as instructed below:

Pipet Volume Range	Set Volume to:	Permitted Ranges
40-200 μL	50 μL	0.049-0.051 g
200-1000 μL	1000 μL	0.990-1.010 g
1000-5000 μL	2000 μL	1.990-2.010 g

2. While wearing gloves, place the appropriate size pipet tip onto the end of the pipet.

3. Using the balance, set for low range (0-30 g), place a weighboat on the balance and tare. Use fresh deionized water and pipet the specified volume into weighboat. Weigh DI water a total of five separate times and average to nearest 0.1 mg and compare this average with the permissible ranges in Step 1. Record all measurements in the instrument calibration logbook.

4. If the mean in Step 3 lies outside of the permitted range, the volume setting should be adjusted according to manufacturer's instructions.

A.3.2 Pipet Operation - Forward Technique

NOTE: Operate the thumb button slowly and steadily. Do not let the thumb button snap back. Deliver the volume smoothly.

1. While wearing gloves, place a clean pipet tip on pipet.

2. Keep the pipet as vertical as possible during uptake of solution. Depress thumb button to first stop. Dip the pipet tip slightly below the solution surface and slowly release the thumb button.

3. Deliver the liquid by gently depressing the thumb button to the first stop. Touch the pipet tip to side of the container (except when preserving aliquots) while simultaneously depressing the thumb button to the second stop. Slowly release the thumb button.

4. Remove the used pipet tip by pressing the tip ejector down. Dispose of the pipet tip in a proper waste receptacle.

A.3.3 Pipet Operation - Reverse Technique

NOTE: Use this technique to pipet viscous liquids.

1. Apply a pipet tip and depress thumb button to second stop. Dip the pipet tip slightly below the surface of the solution and slowly release the thumb button.
2. Deliver the liquid by gently depressing the button to the first stop. Release the thumb button. Remove and dispose of the pipet tip.

A.3.4 Care of Pipets

1. If any liquid is sucked into the barrel, immediately consult the manufacturer's guide and clean as directed. Do not use pipet until it is cleaned.
2. For leakage or inaccuracies refer to the manufacturer's troubleshooting guide.

A.4 Repipet Dispenser Instructions

These instructions are specific to the Reference Lab Industries' Repipet used in the AERP studies. These procedures may be modified for use for other equivalent apparatus. Do not include the drops that are dispensed when pulling up on the Repipet dispenser in the delivery volume.

A.4.1 Calibration of 2.0-mL, 5.0-mL, or 10-mL Repipet Dispensers

1. Set the Repipet to dispense 2.0, 5.0, or 10 mL of solution as directed by manufacturer.
2. Place the weighboat on the balance and tare. Fill the Repipet bottle with DI water and dispense 2.0, 5.0, or 10 mL of DI water into the weighboat.
3. Return the weighboat to the balance and weigh contents. Acceptable limits are:

Repipet	Limits
2.0 mL	2.0 ± 0.02 g
5.0 mL	5.0 ± 0.05 g
10.0 mL	10.0 ± 0.10 g

If weight is outside range, adjust dispenser as directed by manufacturer and recheck.

Appendix B

Direct/Delayed Response Project Blank Data Forms

The Direct/Delayed Response Project forms shown in this appendix are facsimiles of the forms used in the preparation and analytical laboratories.

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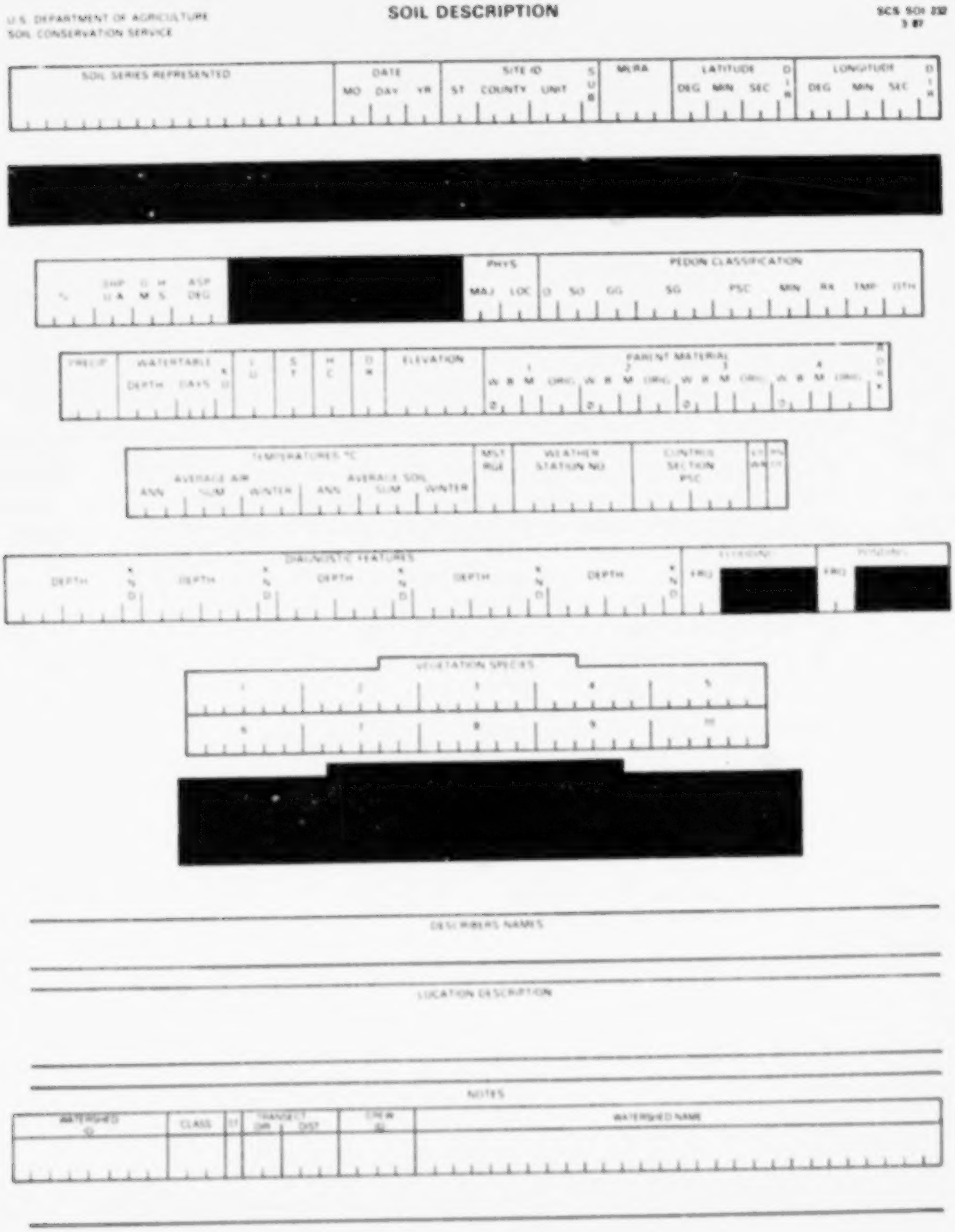

U.S. DEPARTMENT OF AGRICULTURE
SOIL CONSERVATION SERVICE

SOIL DESCRIPTION

SCS SOI 232
3 87

SOIL SERIES REPRESENTED	DATE MO DAY YR	SITE ID ST COUNTY UNIT	SUB	MLRA	LATITUDE DEG MIN SEC	DIR	LONGITUDE DEG MIN SEC	DIR

[redacted]

%	SHP U A	G M	H S	ASP DEG		PHYS MAJ LOC	PEDON CLASSIFICATION O SO GG SG PSC MIN RX TMP OTH
					[redacted]		

PRECIP	WATERTABLE DEPTH DAYS	K D	I U	S T	H C	D R	ELEVATION	PARENT MATERIAL 1 W B M ORG	2 W B M ORG	3 W B M ORG	4 W B M ORG	B D R K

TEMPERATURES °C AVERAGE AIR ANN SUM WINTER	AVERAGE SOIL ANN SUM WINTER	MST RGE	WEATHER STATION NO	CONTROL SECTION PSC	[illegible]	[illegible]

DIAGNOSTIC FEATURES DEPTH	K N D	DEPTH	K N D	DEPTH	K N D	DEPTH	K N D	DEPTH	K N D	[illegible] FRQ		[illegible] FRQ	
											[redacted]		[redacted]

VEGETATION SPECIES

1	2	3	4	5
6	7	8	9	10

[redacted]

DESCRIBERS NAMES

LOCATION DESCRIPTION

NOTES

WATERSHED ID	CLASS	[illegible]	TRANSECT DIR DIST	CREW ID	WATERSHED NAME

Figure B-1. Field data form (1 of 4).

	DEPTH	HORIZON DESIGNATION			THICKNESS			DRY COLOR					MOIST COLOR					TEXTURE	
	UPPER / LOWER	DISC	MASTER LETTER	SUFFIX	AVG.	MAX.	MIN.	LOC	%	HUE	VAL	CHR	LOC	%	HUE	VAL	CHR	CLASS	MOD
1																			
2																			
3																			
4																			
5																			
6																			
7																			
8																			
9																			
10																			

FREE FORM NOTES

	SAMPLE NUMBERS	BULK DENSITY		HORIZON NOTES
		NO	TYP	
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				

Figure B-1. Field data form (2 of 4).

STRUCTURE			CONSISTENCE			MOTTLES						SURFACE FEATURES								BOUNDARY	
GRD	SZ	SHP	a) DRY b) MOIST c) OTHER	a) ST b) PL	CEM	AB	SZ	CON	HUE	VAL	CHR	KND	AB	CN	DST	LOC	HUE	VAL	CHR	BOUNDARY	
			a	a																	1
			b	b																	
			c																		
			a	a																	2
			b	b																	
			c																		
			a	a																	3
			b	b																	
			c																		
			a	a																	4
			b	b																	
			c																		
			a	a																	5
			b	b																	
			c																		
			a	a																	6
			b	b																	
			c																		
			a	a																	7
			b	b																	
			c																		
			a	a																	8
			b	b																	
			c																		
			a	a																	9
			b	b																	
			c																		
			a	a																	10
			b	b																	
			c																		

FREE FORM NOTES

Figure B-1. Field data form (3 of 4).

EFFERVESCENCE	FIELD MEASURED PROPERTIES		FIELD MEASURED PROPERTIES		WETNESS	HYDO COND	ROOTS			PORES				CONCENTRATIONS				ROCK FRAGMENTS				ROCK FRAGMENTS			
CL AG EK	KND	AMOUNT	KND	AMOUNT			QT	SZ	LOC	SHP	QT	SZ	CN	KND	QT	SHP	SZ	KND	%	RND	SZ	KND	%	RND	SZ
	P																								
	C																								
	P																								
	C																								
	P																								
	C																								
	P																								
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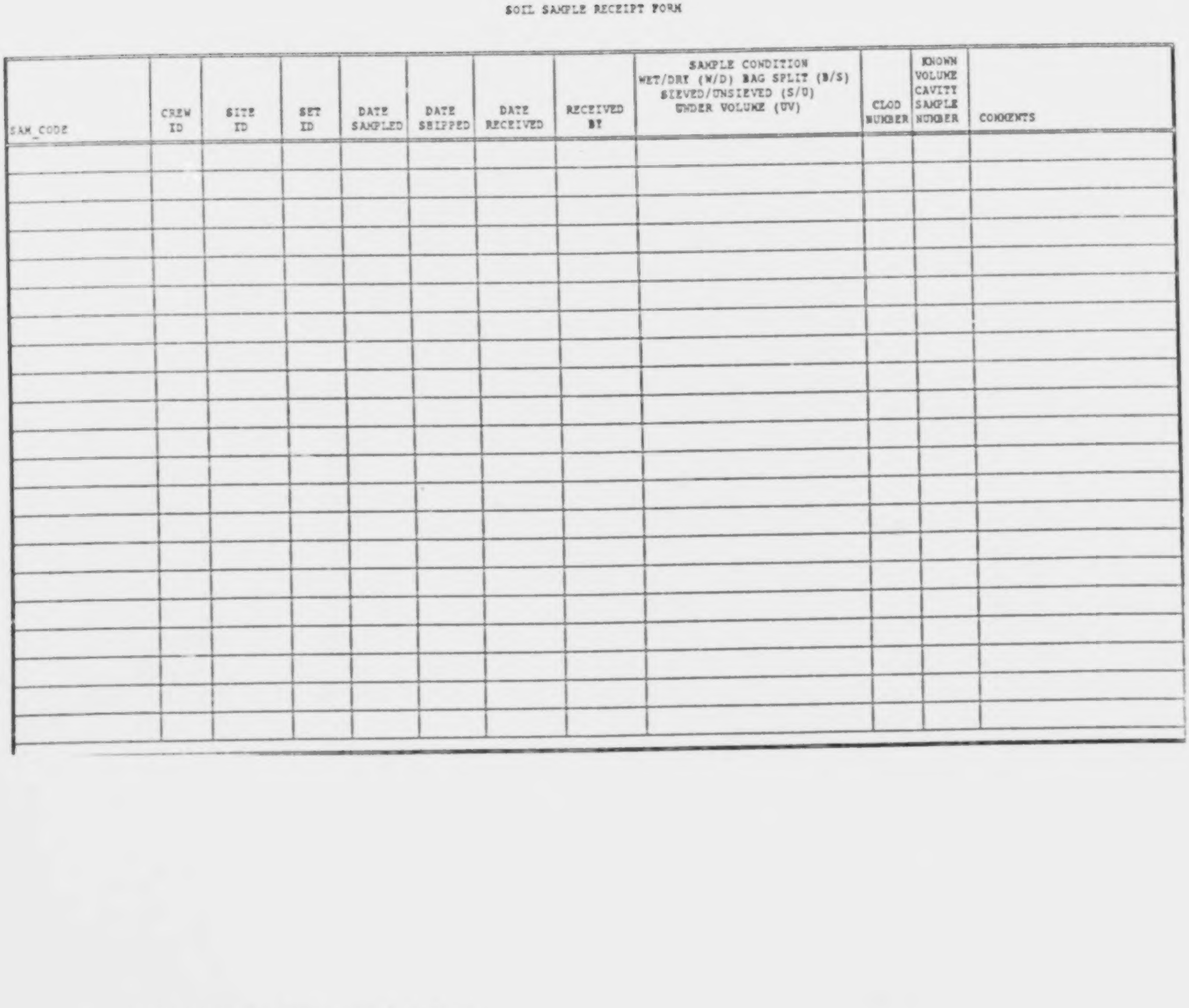
	C																								
	P																								
	C																								
	P																								
	C																								
	P																								
	C																								

FREE FORM NOTES

LOG	
WEATHER	
SET I.D.	
UNDERSTORY VEG	
SLIDES #s PED FACE	OVERSTORY
UNDERSTORY	LANDSCAPE

Figure B-1. Field data form (4 of 4).



SOIL SAMPLE RECEIPT FORM

SAM_CODE	CREW ID	SITE ID	SET ID	DATE SAMPLED	DATE SHIPPED	DATE RECEIVED	RECEIVED BY	SAMPLE CONDITION WET/DRY (W/D) BAG SPLIT (B/S) SIEVED/UNSIEVED (S/U) UNDER VOLUME (UV)	CLOD NUMBER	KNOWN VOLUME CAVITY SAMPLE NUMBER	COMMENTS

Figure B-2. Sample receipt raw data form.

BULK SAMPLE RAW DATA

SAMPLE ID: _ _ _ _ _ _ _ _ _ _ _ _ DATE SAMPLED: ___/___/___
SITE ID: ______________ DATE REC'D: ___/___/___
SET ID: ______________ PROCESS START: ___/___/___
BATCH ID: ______________ PROCESS COMPLETE: ___/___/___

SOIL TYPE: M/O FIELD pH: ______
Initials: ______ Initials: ______

AIR SAMPLE DRYING:

Date	% Moisture	Initials
___/___	________	______
___/___	________	______
___/___	________	______

TOTAL BULK WT:

Date: ___/___/___ ______.____ g Initials: ______

ROCK FRAGMENT WT:

2 to 4.75 mm: ______.____g 4.75 to 20 mm: ______.____g
Date: ___/____/_____ Initials: ______

ENTERED IN COMPUTER: Date: ____/____/_____ Initials:

COMMENTS:

Figure B-3. Bulk sample processing raw data form.

CLOD BULK DENSITY RAW DATA

page ___/___

ALL WEIGHTS RECORDED TO 0.01 GRAMS

SAM_CODE	REP	FLD_DP	FLD_WT moist/dry	LAB_DP	LAB_WT	CLOD_H2O	TEMP C		CRUC NO.	R_FRAG		FLOAT	PROB Y/N	ID	COMMENTS

Figure B-4. Clod bulk density raw data form.

KNOWN VOLUME BULK DENSITY DATA

PAGE ___/___

ALL WEIGHTS RECORDED TO 0.0 GRAMS

SAM_CODE	AIR_WT	OD_WT	R_FRAG	VOL (cc.)	DATE	ID	COMMENTS

Figure B-5. Known volume bulk density raw data form.

pH RAW DATA DATE / /

SAMPLE CODE	SAMP. #	pH	SAMPLE CODE	SAMP. #	pH
Init QCCS			QCCS		
D			D		
QCCS			QCCS		
D			Final QCCS		

Figure B-6. Field-moist pH raw data form.

SAMPLE LOSS ON IGNITION DATA

ALL WEIGHTS REPORTED IN 0.01 GRAMS

SAM_CODE	CRUC. NO.	AIR WT.	O. D. WT.	ASHED WT.	DATE	ID	COMMENTS

Figure B-7. Loss-on-ignition raw data form.

SOIL SAMPLE AIR DRY DETERMINATION

ALL WEIGHTS REPORTED TO 0.01 GRAMS

SAM_CODE	TIN NO.	TIN WT.	AIR DRY (TIN+SOIL)	OVEN DRY (TIN+SOIL)	DATE	ID	COMMENTS

Figure B-8. Air-dry moisture raw data form.

Form # 1

Parameter - MOIST
Air Dry Moisture Percent

Batch # ______
Submission # __
Run # __

Re-Analysis _

Lab Code ______
Date Analysis Started ________
Date Analysis Completed ________
Date Form Completed ________
Lab Manager Initials ____

A	B	C	D
Samp. #	Air Dried Sample Wt. (g) xx.xx	Oven Dried Sample Wt. (g) xx.xx	Calculated Result (%) xx.xx
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
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22			
23			
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26			
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41			
42			

Figure B-9. Form 1, air-dry moisture parameter data.

Form # QC- 1

Parameter - MOIST
Air Dry Moisture Percent

Batch # ______
Submission # __
Run # __

Re-Analysis _

Lab Code ______
Date Analysis Started ________
Date Analysis Completed ________
Date Form Completed ________
Lab Manager Initials ___

Replicates

A Samp. #	B Air Dried Sample Wt. (g) xx.xx	C Oven Dried Sample Wt. (g) xx.xx	D Calculated Result (%) xx.xx	E SD or %RSD xxx.xx

Figure B-10. Form QC-1, quality control data for air-dry moisture content.

Form # 2

Particle Size Parameters
(Raw Data)

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G	H	I	J	K
Samp #	Air Dry Samp. Wt. (g) xx.xx	Treat. Oven Dry Wt. (g) x.xx	Total Sand Wt. (g) x.xx	Sand Very Coarse Wt. (g) x.xx	Sand Coarse Wt. (g) x.xx	Sand Med. Wt. (g) x.xx	Sand Fine Wt. (g) x.xx	Sand Very Fine Wt. (g) x.xx	Pipet Fine Silt + Clay Wt. (g) x.xxxx	Pipet Clay Wt. (g) x.xxxx
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										
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41										
42										
RBK1	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX	XXXXXX		XXXXXXXX

Figure B-11. Form 2, particle size parameters (raw data).

Form # 3

Partical Size Parameters
(Calculated Data)

Batch # _____
Lab Code _____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G	H	I	J	K
Samp. #	Sand	Silt	Clay	Sand Very Coarse	Sand Coarse	Sand Medium	Sand Fine	Sand Very Fine	Silt Coarse	Silt Fine
	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x
1										
2										
3										
4										
5										
6										
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42										

Figure B-12. Form 3, particle size parameters (calculated data).

Form # QC-2

Partical Size Parameters
(Raw Data)

Batch # _____
Lab Code _____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission # __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials _____

Replicates

A	B	C	D	E	F	G	H	I	J	K
Samp # Used xx	Air Dry wt. (g) xx.xx	Treat. Oven Dry wt. (g) xx.x	Total Sand wt. (g) x.xx	Sand Very Coarse wt. (g) x.xx	Sand Coarse wt. (g) x.xx	Sand Medium wt. (g) x.xx	Sand Fine wt. (g) x.xx	Sand Very Fine wt. (g) x.xx	Pipet Fine Silt + Clay wt. (g) x.xxxx	Pipet Clay wt. (g) x.xxxx

QCCS

	B	C	D	E	F	G	H	I	J
	Air Dry wt. (g) xx.xx	Treat. Oven Dry wt. (g) x.xx	Sand Very Coarse wt. (g) x.xx	Sand Coarse wt. (g) x.xx	Sand Medium wt. (g) x.xx	Sand Fine wt. (g) x.xx	Sand Very Fine wt. (g) x.xx	Pipet Fine Silt + Clay wt. (g) x.xxxx	Pipet Clay wt. (g) x.xxxx
True									
High									
Low									
QCCS 1									
QCCS 2									
QCCS 3									
QCCS 4									
QCCS 5									
QCCS 6									
QCCS 7									
QCCS 8									

Figure B-13. Form QC-2, quality control for particle size parameters (raw data).

Form # QC-3

Partical Size Parameters
(Calculated Data)

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission # __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H	I	J	K
Samp. # Used	Sand	Silt	Clay	Sand Very Coarse	Sand Coarse	Sand Medium	Sand Fine	Sand Very Fine	Silt Coarse	Silt Fine
	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
xx	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x

RSD

B	C	D	E	F	G	H	I	J	K
Sand	Silt	Clay	Sand Very Coarse	Sand Coarse	Sand Medium	Sand Fine	Sand Very Fine	Silt Coarse	Silt Fine
(%RSD)	(%RSD)	(%RSD)	(%RSD)	(%RSD)	(%RSD)	(%RSD)	(%RSD)	(%RSD)	(%RSD)
xx.xx	xx.xx	xx.xx	xx.xx	xx.xx	xx.xx	xx.xx	xx.xx	xx.xx	xx.xx

QCCS

	B	C	D	E	F	G	H	I	J	K
	Sand	Silt	Clay	Sand Very Coarse	Sand Coarse	Sand Medium	Sand Fine	Sand Very Fine	Silt Coarse	Silt Fine
	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x	xx.x
True										
High										
Low										
QCCS 1										
QCCS 2										
QCCS 3										
QCCS 4										
QCCS 5										
QCCS 6										
QCCS 7										
QCCS 8										

Figure B-14. Form QC-3, quality control particle size parameters (calculated data).

Form # 4

Parameter - PH_H2O
pH in Water

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D
Samp. #	Sample Wt. (g) xx.x	Solution Vol. (mL) xx.x	Result (pH) x.xx
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28			
29			
30			
31			
32			
33			
34			
35			
36			
37			
38			
39			
40			
41			
42			
RBLK1	XXXXXXXX	XXXXXXXXXX	

Figure B-15. Form 4, pH in water.

Form # 5

Parameter - PH_01M
pH in 0.01M Calcium Chloride

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D
Samp. #	Sample Wt. (g) xx.x	Solution Vol. (mL) xx.x	Result (pH) x.xx
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28			
29			
30			
31			
32			
33			
34			
35			
36			
37			
38			
39			
40			
41			
42			
RBLK1	XXXXXXXX	XXXXXXXXXX	

Figure B-16. Form 5, pH in 0.01 M calcium chloride.

Form # QC-4

Parameter - PH_H2O
pH in Water

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates				
A	B	C	D	E
Samp. # Used xx	Sample Wt. (g) xx.x	Solution Vol. (mL) xx.x	Result (pH) x.xx	SD xxx.xx

QCCS	(pH) x.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

Figure B-17. Form QC-4, quality control parameter pH in water.

Form # QC-5

Parameter - PH_01M
pH in 0.01M Calcium Chloride

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates				
A	B	C	D	E
Samp. # Used	Sample Wt. (g)	Solution Vol. (mL)	Result (pH)	SD
xx	xx.x	xx.x	x.xx	xxx.xx

QCCS	(pH) x.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

Figure B-18. Form QC-5, quality control parameter pH in 0.01 M calcium chloride.

Form # 6A

Parameter - CEC_OAC
Cation Exchange Capacity - Ammonium Acetate
(Flow Injection Analysis)

Batch # ____
Lab Code ____

Submission #
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
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27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-19. Form 6A, cation exchange capacity-ammonium acetate (flow injection analysis).

Form # 6B

Parameter - CEC_OAC
Cation Exchange Capacity - Ammonium Acetate
(Titration Method)

Batch # ___
Lab Code ___

Submission # ___
Orig. Analysis ___
Re-Analysis ___
Re-submission ___

Date Analysis Started ___/___/___
Date Analysis Completed ___/___/___
Date Form Completed ___/___/___
Lab Manager Initials ___

A	B	C	D	E
Samp. #	Sample Wt. (g) x.xx	Titrant Vol. (mL) xx.xx	Acid Normality N x.xxxx	Calculated Result (meq/100g) xxx.xxx
1				
2			XXXXXXXXXX	
3			XXXXXXXXXX	
4			XXXXXXXXXX	
5			XXXXXXXXXX	
6			XXXXXXXXXX	
7			XXXXXXXXXX	
8			XXXXXXXXXX	
9			XXXXXXXXXX	
10			XXXXXXXXXX	
11			XXXXXXXXXX	
12			XXXXXXXXXX	
13			XXXXXXXXXX	
14			XXXXXXXXXX	
15			XXXXXXXXXX	
16			XXXXXXXXXX	
17			XXXXXXXXXX	
18			XXXXXXXXXX	
19			XXXXXXXXXX	
20			XXXXXXXXXX	
21			XXXXXXXXXX	
22			XXXXXXXXXX	
23			XXXXXXXXXX	
24			XXXXXXXXXX	
25			XXXXXXXXXX	
26			XXXXXXXXXX	
27			XXXXXXXXXX	
28			XXXXXXXXXX	
29			XXXXXXXXXX	
30			XXXXXXXXXX	
31			XXXXXXXXXX	
32			XXXXXXXXXX	
33			XXXXXXXXXX	
34			XXXXXXXXXX	
35			XXXXXXXXXX	
36			XXXXXXXXXX	
37			XXXXXXXXXX	
38			XXXXXXXXXX	
39			XXXXXXXXXX	
40			XXXXXXXXXX	
41			XXXXXXXXXX	
42			XXXXXXXXXX	
RBLK1	XXXXXXXX		XXXXXXXXXX	
RBLK2	XXXXXXXX		XXXXXXXXXX	
RBLK3	XXXXXXXX		XXXXXXXXXX	

Figure B-20. Form 6B, cation exchange capacity-ammonium acetate (titration method).

Form # 7A

Parameter - CEC_CL
Cation Exchange Capacity - Ammonium Chloride
(Flow Injection Analysis)

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g)	Final Soln. Vol. (mL)	Aliquot Vol. (mL)	Dilution Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)
	x.xx	xx.x	xx.x	xx.x	xxx.xx	xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
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27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-21. Form 7A, cation exchange capacity-ammonium chloride (flow injection analysis).

Form # 7B

Parameter - CEC_CL
Cation Exchange Capacity - Ammonium Chloride
(Titration Method)

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E
Samp. #	Sample Wt. (g) x.xx	Titrant Vol. (mL) xx.xx	Acid Normality N x.xxxx	Calculated Result (meq/100g) xxx.xxx
1				
2			XXXXXXXXXX	
3			XXXXXXXXXX	
4			XXXXXXXXXX	
5			XXXXXXXXXX	
6			XXXXXXXXXX	
7			XXXXXXXXXX	
8			XXXXXXXXXX	
9			XXXXXXXXXX	
10			XXXXXXXXXX	
11			XXXXXXXXXX	
12			XXXXXXXXXX	
13			XXXXXXXXXX	
14			XXXXXXXXXX	
15			XXXXXXXXXX	
16			XXXXXXXXXX	
17			XXXXXXXXXX	
18			XXXXXXXXXX	
19			XXXXXXXXXX	
20			XXXXXXXXXX	
21			XXXXXXXXXX	
22			XXXXXXXXXX	
23			XXXXXXXXXX	
24			XXXXXXXXXX	
25			XXXXXXXXXX	
26			XXXXXXXXXX	
27			XXXXXXXXXX	
28			XXXXXXXXXX	
29			XXXXXXXXXX	
30			XXXXXXXXXX	
31			XXXXXXXXXX	
32			XXXXXXXXXX	
33			XXXXXXXXXX	
34			XXXXXXXXXX	
35			XXXXXXXXXX	
36			XXXXXXXXXX	
37			XXXXXXXXXX	
38			XXXXXXXXXX	
39			XXXXXXXXXX	
40			XXXXXXXXXX	
41			XXXXXXXXXX	
42			XXXXXXXXXX	
RBLK1	XXXXXXXX		XXXXXXXXXX	
RBLK2	XXXXXXXX		XXXXXXXXXX	
RBLK3	XXXXXXXX		XXXXXXXXXX	

Figure B-22. Form 7B, cation exchange capacity-ammonium chloride (titration method).

Form # QC-6A

Parameter - CEC OAC
Cation Exchangable Capacity In Ammonium Acetate
(Flow Injection Analysis)

Batch # ___
Lab Code ___

Submission # ___
Orig. Analysis ___
Re-Analysis ___
Re-submission # ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ___

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Final Soln. Vol. (mL)	Aliquot Vol. (mL)	Dilution Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)	RSD (%)
xx	x.xx	xx.x	xx.x	xx.x	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Dilut. Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xx.x	xx.x	xxxx.x	xx.x	xx.x	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (mg/L) xxx.xx

Figure B-23. Form QC-6A, quality control parameter cation exchangeable capacity-ammonium acetate (flow injection analysis).

Form # QC-6B

Parameter - CEC_OAC
Cation Exchange Capacity in Ammonium Acetate
(Titration Method)

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission # __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F
Samp. # Used	Sample Wt.	Titrant Vol.	Acid Normality	Calculated Results	RSD
	(g)	(mL)	N	(meq/100g)	(%)
xx	x.xx	xx.xx	x.xxxx	xxx.xxx	xxx.xx

Matrix Spikes

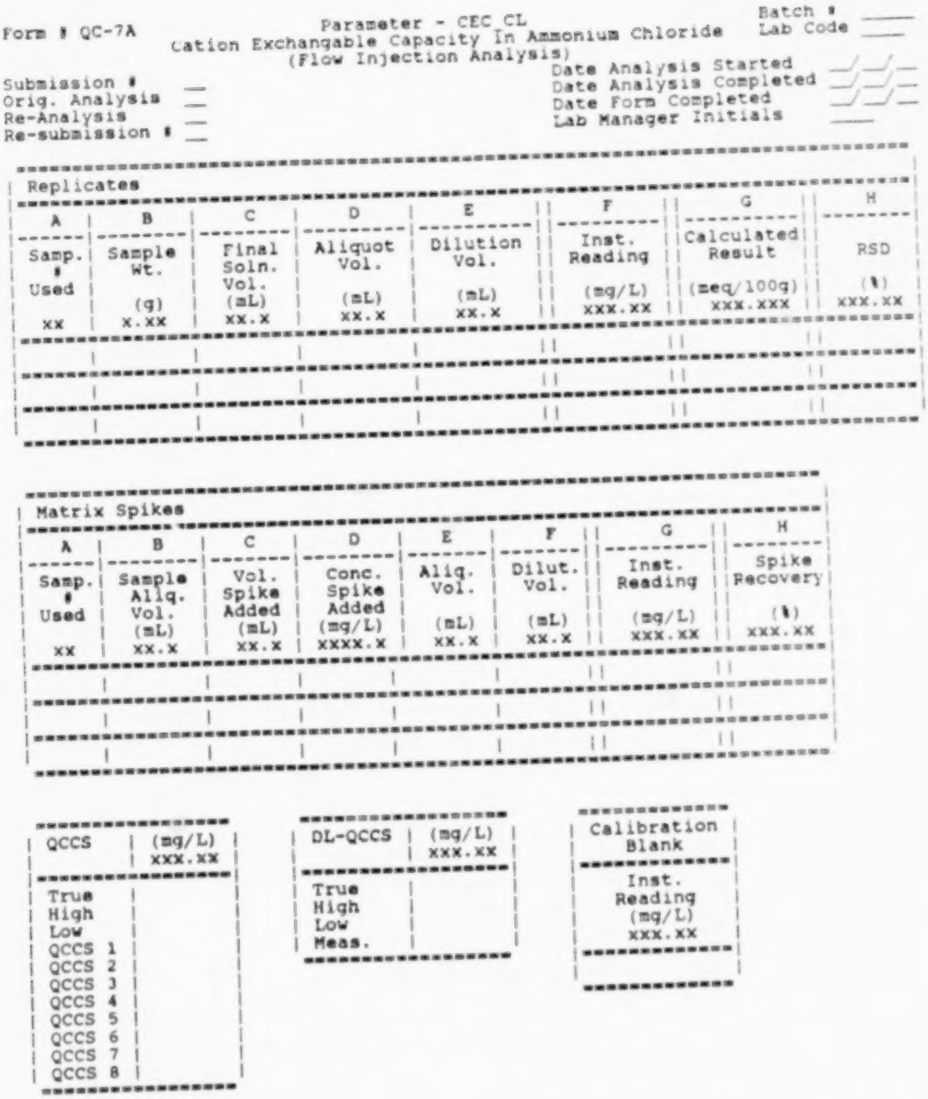
A	B	C	D	E	F	G
Samp. #	Vol. Spike Added	Conc. Spike Added	Titrant Vol.	Acid Normality	Calc. Results	Spike Recovery
	(mL)	(meq)	(mL)	N	(meq)	(%)
xx	x.xx	xx.xxx	xx.xx	x.xxxx	xxx.xxx	xxx.xx

QCCS	(meq) xxx.xxx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(meq) xxx.xxx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (meq) xxx.xxx

Figure B-24. Form QC-6B, quality control parameter cation exchangeable capacity-ammonium acetate (titration method).



Form # QC-7A

Parameter - CEC CL
Cation Exchangable Capacity In Ammonium Chloride
(Flow Injection Analysis)

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission # __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Final Soln. Vol. (mL)	Aliquot Vol. (mL)	Dilution Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)	RSD (%)
xx	x.xx	xx.x	xx.x	xx.x	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Dilut. Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xx.x	xx.x	xxxx.x	xx.x	xx.x	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (mg/L) xxx.xx

Figure B-25. Form QC-7A, quality control parameter cation exchangeable capacity-ammonium chloride (flow injection analysis).

Form # QC-7B

Parameter - CEC CL
Cation Exchange Capacity - Ammonium Chloride
(Titration Method)

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission # __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F
Samp. # Used	Sample Wt. (g)	Titrant Vol. (mL)	Acid Normality N	Calculated Results (meq/100g)	RSD (%)
xx	x.xx	xx.xx	x.xxxx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G
Samp. #	Vol. Spike Added (mL)	Conc. Spike Added (meq)	Titrant Vol. (mL)	Acid Normality N	Calc. Results (meq)	Spike Recovery (%)
xx	x.xx	xx.xxx	xx.xx	x.xxxx	xxx.xxx	xxx.xx

QCCS	(meq) xxx.xxx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(meq) xxx.xxx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (meq) xxx.xxx

Figure B-26. Form QC-7B, quality control parameter cation exchangeable capacity-ammonium chloride (titration method).

Form # 8

Parameter - CA_OAC
Calcium in Ammonium Acetate

Batch ____
Lab Code ____

Submission #
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-27. Form 6, calcium in ammonium acetate.

Form # 9

Parameter - MG_OAC
Magnesium in Ammonium Acetate

Batch # ____
Lab Code ____

Submission #
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-28. Form 9, magnesium in ammonium acetate.

Form # 10

Parameter - K_OAC
Potassium in Ammonium Acetate

Batch # ___
Lab Code ___

Submission #
Orig. Analysis ___
Re-Analysis ___
Re-submission ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ___

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-29. Form 10, potassium in ammonium acetate.

Form # 11

Parameter - NA_OAC
Sodium in Ammonium Acetate

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
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25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-30. Form 11, sodium in ammonium acetate.

Form # QC-8

Parameter - CA_OAC
Calcium in Ammonium Acetate

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission # __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx	RSD (%) xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Aliq. Vol. (mL) xx.x	Vol. Spike Added (mL) xx.x	Conc. Spike Added (mg/L) xxxx.x	Aliq. Vol. (mL) xx.x	Dilut. Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Spike Recovery (%) xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (mg/L) xxx.xx

Figure B-31. Form QC-8, quality control calcium in ammonium acetate.

Form # QC-9

Parameter - MG_OAC
Magnesium in Ammonium Acetate

Batch # ____
Lab Code ____

Submission # ___
Orig. Analysis ___
Re-Analysis ___
Re-submission # ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx	RSD (%) xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Aliq. Vol. (mL) xx.x	Vol. Spike Added (mL) xx.x	Conc. Spike Added (mg/L) xxxx.x	Aliq. Vol. (mL) xx.x	Dilut. Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Spike Recovery (%) xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (mg/L) xxx.xx

Figure B-32. Form QC-9, quality control magnesium in ammonium acetate.

Form # QC-10

Parameter - K_OAC
Potassium in Ammonium Acetate

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission # __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Final Soln. Vol. (mL)	Aliquot Vol. (mL)	Dilution Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)	RSD (%)
xx	x.xx	xx.x	xx.x	xx.x	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Dilut. Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xx.x	xx.x	xxxx.x	xx.x	xx.x	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (mg/L) xxx.xx

Figure B-33. Form QC-10, quality control potassium in ammonium acetate.

Form # QC-11

Parameter - NA_OAC
Sodium in Ammonium Acetate

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission # __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Final Soln. Vol. (mL)	Aliquot Vol. (mL)	Dilution Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)	RSD (%)
xx	x.xx	xx.x	xx.x	xx.x	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Dilut. Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xx.x	xx.x	xxxx.x	xx.x	xx.x	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (mg/L) xxx.xx

Figure B-34. Form QC-11, quality control sodium in ammonium acetate.

Form # 12

Parameter - CA_CL
Calcium in Ammonium Chloride

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
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27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-35. Form 12, calcium in ammonium chloride.

Form # 13

Parameter - MG_CL
Magnesium in Ammonium Chloride

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
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27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-36. Form 13, magnesium in ammonium chloride.

Form # 14

Parameter - K_CL
Potassium in Ammonium Chloride

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
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29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-37. Form 14, potassium in ammonium chloride.

Form # 15

Parameter - NA_CL
Sodium in Ammonium Chloride

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
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39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-38. Form 15, sodium in ammonium chloride.

Form # 16

Parameter - AL_CL
Aluminum in Ammonium Chloride

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
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33						
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35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-39. Form 16, aluminum in ammonium chloride.

Form # QC-12

Parameter - CA_CL
Calcium in Ammonium Chloride

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission # __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Final Soln. Vol. (mL)	Aliquot Vol. (mL)	Dilution Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)	RSD (%)
xx	x.xx	xx.x	xx.x	xx.x	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Dilut. Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xx.x	xx.x	xxxx.x	xx.x	xx.x	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (mg/L) xxx.xx

Figure B-40. Form QC-12, quality control calcium in ammonium chloride.

Form # QC-13
Parameter - MG_CL
Magnesium in Ammonium Chloride
Batch # ____
Lab Code ____

Submission #
Orig. Analysis __
Re-Analysis __
Re-submission # __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Final Soln. Vol. (mL)	Aliquot Vol. (mL)	Dilution Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)	RSD (%)
xx	x.xx	xx.x	xx.x	xx.x	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Dilut. Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xx.x	xx.x	xxxx.x	xx.x	xx.x	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (mg/L) xxx.xx

Figure B-41. Form QC-13, quality control magnesium in ammonium chloride.

Form # QC-14

Parameter - K_CL
Potassium in Ammonium Chloride

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission # __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Final Soln. Vol. (mL)	Aliquot Vol. (mL)	Dilution Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)	RSD (%)
xx	x.xx	xx.x	xx.x	xx.x	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Dilut. Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xx.x	xx.x	xxxx.x	xx.x	xx.x	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (mg/L) xxx.xx

Figure B-42. Form QC-14, quality control potassium in ammonium chloride.

Form # QC-15

Parameter - NA CL
Sodium in Ammonium Chloride

Batch # ____
Lab Code ____

Submission #
Orig. Analysis ___
Re-Analysis ___
Re-submission # ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Final Soln. Vol. (mL)	Aliquot Vol. (mL)	Dilution Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)	RSD (%)
xx	x.xx	xx.x	xx.x	xx.x	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Dilut. Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xx.x	xx.x	xxxx.x	xx.x	xx.x	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (mg/L) xxx.xx

Figure B-43. Form QC-15, quality control sodium in ammonium chloride.

Form # QC-16

Parameter - AL_CL
Aluminum in Ammonium Chloride

Batch # ____
Lab Code ____

Submission # __
Orig. Analysis __
Re-Analysis __
Re-submission # __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Wt. (g) x.xx	Final Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.x	Dilution Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx	RSD (%) xxx.xx

Matrix Spikes

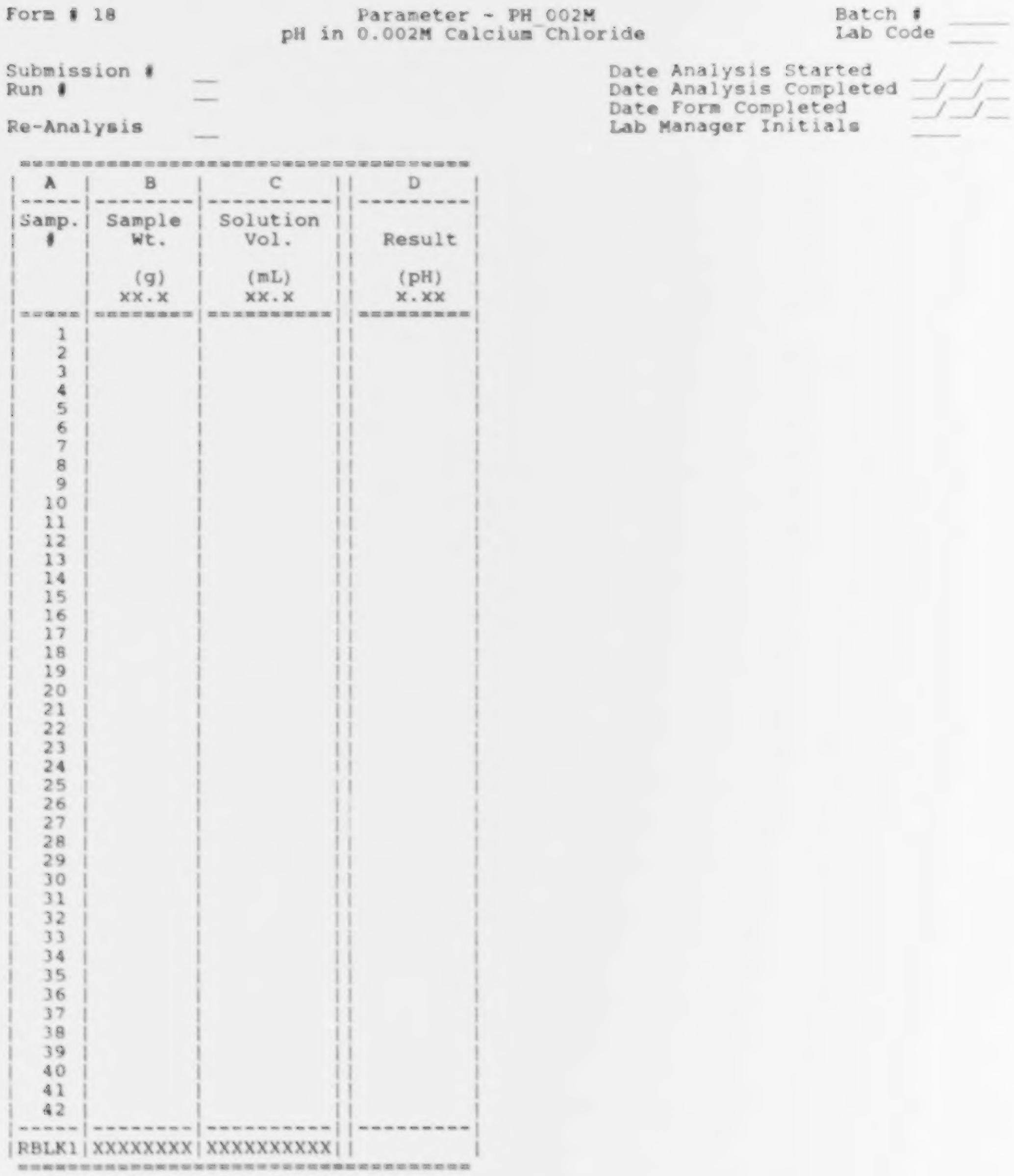
A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Aliq. Vol. (mL) xx.x	Vol. Spike Added (mL) xx.x	Conc. Spike Added (mg/L) xxxx.x	Aliq. Vol. (mL) xx.x	Dilut. Vol. (mL) xx.x	Inst. Reading (mg/L) xxx.xx	Spike Recovery (%) xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calibration Blank
Inst. Reading (mg/L) xxx.xx

Figure B-44. Form QC-16, quality control aluminum in ammonium chloride.



Form # 18

Parameter - PH_002M
pH in 0.002M Calcium Chloride

Batch # ___
Lab Code ___

Submission # ___
Run # ___

Re-Analysis ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ___

A	B	C	D
Samp. #	Sample Wt. (g) xx.x	Solution Vol. (mL) xx.x	Result (pH) x.xx
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
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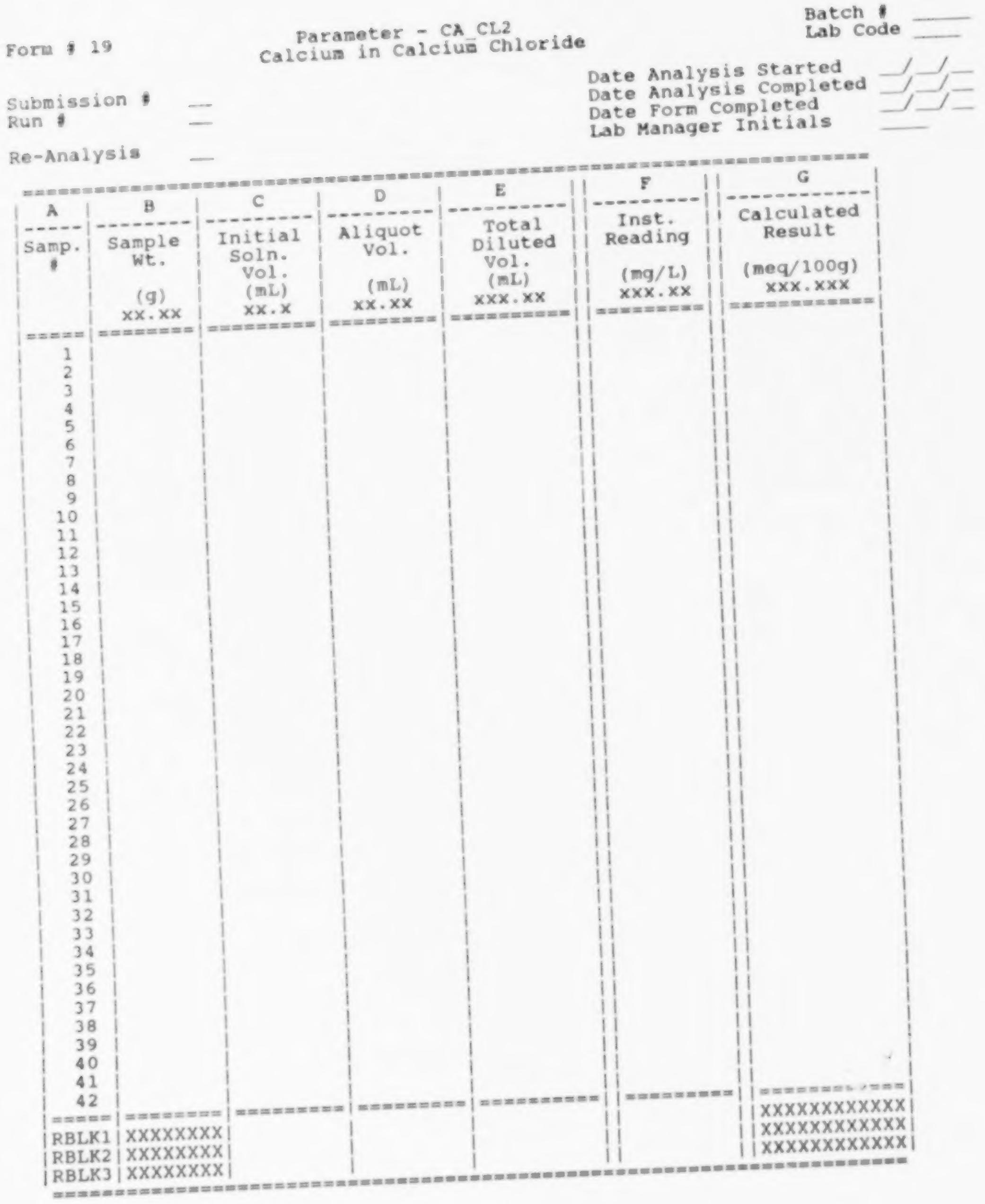
28			
29			
30			
31			
32			
33			
34			
35			
36			
37			
38			
39			
40			
41			
42			
RBLK1	XXXXXXXX	XXXXXXXXXX	

Figure B-45. Form 18, pH in 0.002 M calcium chloride.



Form # 19

Parameter - CA_CL2
Calcium in Calcium Chloride

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) xx.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
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24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-46. Form 19, calcium in 0.002 M calcium chloride.

Form # 20

Parameter - MG_CL2
Magnesium in Calcium Chloride

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) xx.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
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31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-47. Form 20, magnesium in 0.002 M calcium chloride.

Form # 21

Parameter - K_CL2
Potassium in Calcium Chloride

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) xx.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
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31						
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33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-48. Form 21, potassium in 0.002 M calcium chloride.

Form # 22

Parameter - NA_CL2
Sodium in Calcium Chloride

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) xx.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
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16						
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34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-49. Form 22, sodium in 0.002 M calcium chloride.

Form # 23

Parameter - FE CL2
Iron in Calcium Chloride

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) xx.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-50. Form 23, iron in 0.002 M calcium chloride.

Form # 24

Parameter - AL CL2
Aluminum in Calcium Chloride

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g)	Initial Soln. Vol. (mL)	Aliquot Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)
	xx.xx	xx.x	xx.xx	xxx.xx	xxx.xx	xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-51. Form 24, aluminum in 0.002 M calcium chloride.

Form # QC-18

Parameter - PH_002M
pH in 0.002M Calcium Chloride

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates				
A	B	C	D	E
Samp. # Used xx	Sample Wt. (g) xx.x	Solution Vol. (mL) xx.x	Result (pH) x.xx	SD xxx.xx

QCCS	(pH) x.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

Figure B-52. Form QC-18, quality control pH in 0.002 M calcium chloride.

Form # QC-19

Parameter - CA_CL2
Calcium in Calcium_Chloride

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Initial Soln. Vol. (mL)	Aliquot Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)	SD or % RSD
xx	xx.xx	xx.x	xx.xx	xxx.xx	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Tot. Diluted Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xx.xx	xx.xxx	xxxx.x	xx.xx	xxx.xx	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Spike Solution
Inst. Reading (mg/L) xxx.xx

Figure B-53. Form QC-19, quality control calcium in 0.002 M calcium chloride.

Form # QC-20

Parameter - MG_CL2
Magnesium in Calcium Chloride

Batch # ____
Lab Code ____

Submission # ___
Run # ___

Re-Analysis ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Initial Soln. Vol. (mL)	Aliquot Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)	SD or % RSD
xx	xx.xx	xx.x	xx.xx	xxx.xx	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Tot. Diluted Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xx.xx	xx.xxx	xxxx.x	xx.xx	xxx.xx	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-54. Form QC-20, quality control magnesium in 0.002 M calcium chloride.

Form # QC-21

Parameter - K_CL2
Potassium in Calcium Chloride

Batch # ____
Lab Code ____

Submission # ____
Run # ____
Re-Analysis ____

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Initial Soln. Vol. (mL)	Aliquot Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)	SD or % RSD
xx	xx.xx	xx.x	xx.xx	xxx.xx	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Tot. Diluted Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xx.xx	xx.xxx	xxxx.x	xx.xx	xxx.xx	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-55. Form QC-21, quality control potassium in 0.002 M calcium chloride.

Form # QC-22

Parameter - NA CL2
Sodium in Calcium Chloride

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Wt. (g) xx.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx	SD or % RSD xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Aliq. Vol. (mL) xx.xx	Vol. Spike Added (mL) xx.xxx	Conc. Spike Added (mg/L) xxxx.x	Aliq. Vol. (mL) xx.xx	Tot. Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Spike Recovery (%) xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-56. Form QC-22, quality control sodium in 0.002 M calcium chloride.

Form # QC-23

Parameter - FE CL2
Iron in Calcium Chloride

Batch # ____
Lab Code ____

Submission # ___
Run # ___

Re-Analysis ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Initial Soln. Vol. (mL)	Aliquot Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (meq/100g)	SD or % RSD
xx	xx.xx	xx.x	xx.xx	xxx.xx	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Tot. Diluted Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xx.xx	xx.xxx	xxxx.x	xx.xx	xxx.xx	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-57. Form QC-23, quality control iron in 0.002 M calcium chloride.

Form # QC-24

Parameter - AL_CL2
Aluminum in Calcium Chloride

Batch # _____
Lab Code _____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials _____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Wt. (g) xx.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (meq/100g) xxx.xxx	SD or % RSD xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Aliq. Vol. (mL) xx.xx	Vol. Spike Added (mL) xx.xxx	Conc. Spike Added (mg/L) xxxx.x	Aliq. Vol. (mL) xx.xx	Tot. Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Spike Recovery (%) xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-58. Form QC-24, quality control aluminum in 0.002 M calcium chloride.

Form # 17

Parameter - AC_BACL
Barium Chloride - TEA Acidity

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Extract Vol. (mL) xx.x	Titrant Vol. (mL) xxx.xx	Acid Normality N x.xxxx	Calculated Result (meq/100g) xxx.xxx	Calculated Reagent Blank (meq) xxx.xxx
1						XXXXXXXXXXXXXXX
2				XXXXXXXXXX		XXXXXXXXXXXXXXX
3				XXXXXXXXXX		XXXXXXXXXXXXXXX
4				XXXXXXXXXX		XXXXXXXXXXXXXXX
5				XXXXXXXXXX		XXXXXXXXXXXXXXX
6				XXXXXXXXXX		XXXXXXXXXXXXXXX
7				XXXXXXXXXX		XXXXXXXXXXXXXXX
8				XXXXXXXXXX		XXXXXXXXXXXXXXX
9				XXXXXXXXXX		XXXXXXXXXXXXXXX
10				XXXXXXXXXX		XXXXXXXXXXXXXXX
11				XXXXXXXXXX		XXXXXXXXXXXXXXX
12				XXXXXXXXXX		XXXXXXXXXXXXXXX
13				XXXXXXXXXX		XXXXXXXXXXXXXXX
14				XXXXXXXXXX		XXXXXXXXXXXXXXX
15				XXXXXXXXXX		XXXXXXXXXXXXXXX
16				XXXXXXXXXX		XXXXXXXXXXXXXXX
17				XXXXXXXXXX		XXXXXXXXXXXXXXX
18				XXXXXXXXXX		XXXXXXXXXXXXXXX
19				XXXXXXXXXX		XXXXXXXXXXXXXXX
20				XXXXXXXXXX		XXXXXXXXXXXXXXX
21				XXXXXXXXXX		XXXXXXXXXXXXXXX
22				XXXXXXXXXX		XXXXXXXXXXXXXXX
23				XXXXXXXXXX		XXXXXXXXXXXXXXX
24				XXXXXXXXXX		XXXXXXXXXXXXXXX
25				XXXXXXXXXX		XXXXXXXXXXXXXXX
26				XXXXXXXXXX		XXXXXXXXXXXXXXX
27				XXXXXXXXXX		XXXXXXXXXXXXXXX
28				XXXXXXXXXX		XXXXXXXXXXXXXXX
29				XXXXXXXXXX		XXXXXXXXXXXXXXX
30				XXXXXXXXXX		XXXXXXXXXXXXXXX
31				XXXXXXXXXX		XXXXXXXXXXXXXXX
32				XXXXXXXXXX		XXXXXXXXXXXXXXX
33				XXXXXXXXXX		XXXXXXXXXXXXXXX
34				XXXXXXXXXX		XXXXXXXXXXXXXXX
35				XXXXXXXXXX		XXXXXXXXXXXXXXX
36				XXXXXXXXXX		XXXXXXXXXXXXXXX
37				XXXXXXXXXX		XXXXXXXXXXXXXXX
38				XXXXXXXXXX		XXXXXXXXXXXXXXX
39				XXXXXXXXXX		XXXXXXXXXXXXXXX
40				XXXXXXXXXX		XXXXXXXXXXXXXXX
41				XXXXXXXXXX		XXXXXXXXXXXXXXX
42				XXXXXXXXXX		XXXXXXXXXXXXXXX
RBLK1	XXXXXXXX			XXXXXXXXXX	XXXXXXXXXXXX	
RBLK2	XXXXXXXX			XXXXXXXXXX	XXXXXXXXXXXX	
RBLK3	XXXXXXXX			XXXXXXXXXX	XXXXXXXXXXXX	

Figure B-59. Form 17, barium chloride-TEA acidity.

Batch # ___
Lab Code ___

Form # QC-17

Parameter - AC BACL
Barium Chloride-TEA Acidity

Submission # ___
Run # ___

Re-Analysis ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ___

Replicates					
A	B	C	D	E	F
Samp. # Used	Sample Wt. (g)	Titrant Vol. (mL)	Acid Normality N	Calculated Result (meq/100g)	SD or % RSD
xx	x.xx	xxx.xx	x.xxxx	xxx.xxx	xxx.xx

QCCS	(mL) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mL) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mL) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-60. Form QC-17, quality control barium chloride-TEA acidity.

Form # 25

Parameter - FE_PYP
Pyrophosphate Extractable Iron

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g)	Initial Soln. Vol. (mL)	Aliquot Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (wt. %)
	x.xx	xxx.x	xxx.xx	xxx.xx	xxx.xx	xx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-61. Form 25, pyrophosphate extractable iron.

Form # 26

Parameter - AL_PYP
Pyrophosphate Extractable Aluminum

Batch # _____
Lab Code _____

Submission # ___
Run # ___

Re-Analysis ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials _____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xxx.x	Aliquot Vol. (mL) xxx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (wt. %) xx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
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23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-62. Form 26, pyrophosphate extractable aluminum.

Form # 27

Parameter - FE_AO
Acid Oxalate Extractable Iron

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xxx.x	Aliquot Vol. (mL) xxx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (wt. %) xx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-63. Form 27, acid oxalate extractable iron.

Form # 28

Parameter - AL AO
Acid Oxalate Extractable Aluminum

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xxx.x	Aliquot Vol. (mL) xxx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (wt. %) xx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-64. Form 28, acid oxalate extractable aluminum.

Form # 29

Parameter - SI AO
Acid Oxalate Extractable Silicon

Batch # ____
Lab Code ____

Submission # ____
Run # ____

Re-Analysis ____

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xxx.x	Aliquot Vol. (mL) xxx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (wt. %) xx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
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28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXX

Figure B-65. Form 29, acid oxalate extractable silicon.

Form # 30

Parameter - FE_CD
Citrate Dithionite Extractable Iron

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xxx.x	Aliquot Vol. (mL) xxx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (wt. %) xx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
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26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-66. Form 30, citrate dithionite extractable iron.

Form # 31

Parameter - AL_CD
Citrate Dithionite Extractable Aluminum

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xxx.x	Aliquot Vol. (mL) xxx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (wt. %) xx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-67. Form 31, citrate dithionite extractable aluminum.

Form # QC-25

Parameter - FE PYP
Pyrophosphate Extractable Iron

Batch # ____
Lab Code ____

Submission # ____
Run # ____

Re-Analysis ____

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Wt. (g) x.xx	Init. Soln. Vol. (mL) xxx.x	Aliq. Vol. (mL) xxx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Calculated Result (wt. %) xx.xxx	SD or % RSD xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Aliq. Vol. (mL) xxx.xx	Vol. Spike Added (mL) xx.xxx	Conc. Spike Added (mg/L) xxxx.x	Aliq. Vol. (mL) xxx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg/L) xxx.xx	Spike Recovery (%) xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-68. Form QC-25, quality control pyrophosphate extractable iron.

Form # QC-26

Parameter - AL PYP
Pyrophosphate Extractable Aluminum

Batch # _____
Lab Code _____

Submission # ___
Run # ___

Re-Analysis ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials _____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Init. Soln. Vol. (mL)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (wt. %)	SD or % RSD
xx	x.xx	xxx.x	xxx.xx	xxx.xx	xxx.xx	xx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xxx.xx	xx.xxx	xxxx.x	xxx.xx	xxx.xx	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-69. Form QC-26, quality control pyrophosphate extractable aluminum.

Form # QC-27

Parameter - FE_AO
Acid Oxalate Extractable Iron

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Init. Soln. Vol. (mL)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (wt. %)	SD or % RSD
xx	x.xx	xxx.x	xxx.xx	xxx.xx	xxx.xx	xx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xxx.xx	xx.xxx	xxxx.x	xxx.xx	xxx.xx	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-70. Form QC-27, quality control acid oxalate extractable iron.

Form # QC-28

Parameter - AL AO
Acid Oxalate Extractable Aluminum

Batch # ____
Lab Code ____

Submission # ___
Run # ___

Re-Analysis ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Init. Soln. Vol. (mL)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (wt. %)	SD or % RSD
xx	x.xx	xxx.x	xxx.xx	xxx.xx	xxx.xx	xx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xxx.xx	xx.xxx	xxxx.x	xxx.xx	xxx.xx	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-71. Form QC-28, quality control acid oxalate extractable aluminum.

Form # QC-29

Parameter - SI AO
Acid Oxalate Extractable Silicon

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Init. Soln. Vol. (mL)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (wt. %)	SD or % RSD
xx	x.xx	xxx.x	xxx.xx	xxx.xx	xxx.xx	xx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xxx.xx	xx.xxx	xxxx.x	xxx.xx	xxx.xx	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-72. Form QC-29, quality control acid oxalate extractable silicon.

Form # QC-30

Parameter - FE_CD
Citrate Dithionite Extractable Iron

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Init. Soln. Vol. (mL)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (wt. %)	SD or % RSD
xx	x.xx	xxx.x	xxx.xx	xxx.xx	xxx.xx	xx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xxx.xx	xx.xxx	xxxx.x	xxx.xx	xxx.xx	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-73. Form QC-30, quality control citrate dithionite extractable iron.

Form # QC-31

Parameter - AL_CD
Citrate Dithionite Extractable Aluminum

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Sample Wt. (g)	Init. Soln. Vol. (mL)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Calculated Result (wt. %)	SD or % RSD
xx	x.xx	xxx.x	xxx.xx	xxx.xx	xxx.xx	xx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg/L)	Spike Recovery (%)
xx	xxx.xx	xx.xxx	xxxx.x	xxx.xx	xxx.xx	xxx.xx	xxx.xx

QCCS	(mg/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-74. Form QC-31, quality control citrate dithionite extractable aluminum.

Form # 32

Parameter - SO4 H2O
Water Extractable Sulfate

Batch # ___
Lab Code ___

Submission # ___
Run # ___

Re-Analysis ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ___

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xxx.x	Aliquot Vol. (mL) xxx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xx	Calculated Result (mg S/kg) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-75. Form 32, water extractable sulfate.

Form # 33

Parameter - SO4_PO4
Phosphate Extractable Sulfate

Batch # ____
Lab Code ____

Submission # __
Run # __
Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	* Final Soln. Vol. (mL) xxx.x	Aliquot Vol. (mL) xxx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xx	Calculated Result (mg S/kg) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-76. Form 33, phosphate extractable sulfate.

Form # QC-32

Parameter - SO4 H2O
Water Extractable Sulfate

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Samp. Wt. (g)	Initial Soln. Vol. (mL)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg S/L)	Calculated Results (mg S/kg)	SD or % RSD
xx	x.xx	xxx.x	xxx.xx	xxx.xx	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg S/L)	Spike Recovery (%)
xx	xxx.xx	xx.xxx	xxxx.x	xxx.xx	xxx.xx	xxx.xx	xxx.xx

QCCS	(mg S/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg S/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg S/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-77. Form QC-32, quality control water extractable sulfate.

Form # QC-33

Parameter - SO4_PO4
Phosphate Extractable Sulfate

Batch # ____
Lab Code ____

Submission # ___
Run # ___

Re-Analysis ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Samp. Wt. (g)	Initial Soln. Vol. (mL)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg S/L)	Calculated Results (mg S/kg)	SD or % RSD
xx	x.xx	xxx.x	xxx.xx	xxx.xx	xxx.xx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg S/L)	Spike Recovery (%)
xx	xxx.xx	xx.xxx	xxxx.x	xxx.xx	xxx.xx	xxx.xx	xxx.xx

QCCS	(mg S/L) xxx.xx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg S/L) xxx.xx
True	
High	
Low	
Meas.	

Calib. Blank	(mg S/L) xxx.xx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Figure B-78. Form QC-33, quality control phosphate extractable sulfate.

DIRECT/DELAYED RESPONSE PROJECT (DDRP) SOIL SURVEY
FORM 113

QUALITY CONTROL: ION CHROMATOGRAPHY RESOLUTION TEST

LAB NAME ______________________________
BATCH ID ______________________ DATE OF ANALYSIS ____________
MM/DD/YR

LAB MANAGER'S SIGNATURE ______________________________

IC Make and Model: ____________________

	Concentration (mg/L)	Peak Area (integrator units)	Peak Height (cm)
SO_4^{2-}			
PO_4^{3-}			
NO_3^-			

Column Back Pressure (at max. of stroke): ____________________ psi

Flow Rate: ____________ mL/min

Column Model: ________________ Date of Purchase: ____________

Column Manufacturer: ______________________

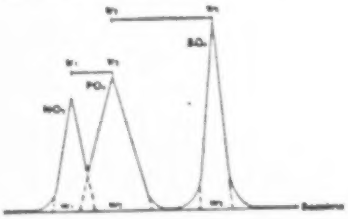
Column Serial No: ______________________

Precolumn in system ___ Yes ___ No

Percentage Resolution:
*100 x $2(tr_2-tr_1)/(W_1+W_2)$ NO_3 - PO_4 ____________
100 x $2(tr_3-tr_2)/(w_2+W_3)$ PO_4 - SO_4 ____________
100 x $2(tr_3-tr_1)/(w_1+W_3)$ NO_3 - SO_4 ____________

The resolution must be greater than 60%.

Test Chromatogram:



(FACSIMILE)

*Calculations may change if order of elution is different from test chromatogram.

Figure B-79. Form IC, quality control: Ion chromotography resolution test.

Form # 34

Parameter - SO4_0
Zero mg S/L Isotherm_Parameter

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Calculated Result (mg S/L) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-80. Form 34, 0 mg S/L Isotherm.

Form # 35

Parameter - SO4_2
Two mg S/L Isotherm Prameter

Batch # ____
Lab Code ____

Submission # ___
Run # ___

Re-Analysis ___

Date Analysis Started ___/___/___
Date Analysis Completed ___/___/___
Date Form Completed ___/___/___
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Calculated Result (mg S/L) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
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22						
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24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-81. Form 35, 2 mg S/L Isotherm.

orm # 36

Parameter - SO4_4
Four mg S/L Isotherm Parmeter

Batch # ____
Lab Code ____

ubmission # __
un # __

e-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Calculated Result (mg S/L) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-82. Form 36, 4 mg S/L Isotherm.

Form # 37

Parameter - SO4 8
Eight mg S/L Isotherm Parameter

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Calculated Result (mg S/L) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
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35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-83. Form 37, 8 mg S/L Isotherm.

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Form # 38

Parameter - SO4_16
Sixteen mg S/L Isotherm Parameter

Batch # _____
Lab Code _____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Calculated Result (mg S/L) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
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34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXX

Figure B-84. Form 38, 16 mg S/L Isotherm.

Form # 39

Parameter - SO4_32
Thirty-two mg S/L Isotherm Parameter

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

A	B	C	D	E	F	G
Samp. #	Sample Wt. (g) x.xx	Initial Soln. Vol. (mL) xx.x	Aliquot Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Calculated Result (mg S/L) xxx.xxx
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
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30						
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32						
33						
34						
35						
36						
37						
38						
39						
40						
41						
42						
RBLK1	XXXXXXXX					XXXXXXXXXXXX
RBLK2	XXXXXXXX					XXXXXXXXXXXX
RBLK3	XXXXXXXX					XXXXXXXXXXXX

Figure B-85. Form 39, 32 mg S/L Isotherm.

Form # QC-34

Parameter - SO4 0
Zero mg S/L Isotherm Parameter

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used xx	Samp. Wt. (g) x.xx	Initial Soln. Vol. (mL) xx.x	Aliq. Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Calculated Results (mg S/kg) xxx.xxx	SD or % RSD xxx.xx

QCCS	(mg S/L) xxx.xxx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg S/L) xxx.xxx
True	
High	
Low	
Meas.	

Calib. Blank	(mg S/L) xxx.xxx
CBLK1	
CBLK2	
CBLK3	
CBLK4	
CBLK5	
CBLK6	
CBLK7	
CBLK8	

Spike Solution
Inst. Reading (mg S/L) xxx.xxx

Figure B-86. Form QC-34, quality control zero mg S/L isotherm parameter.

Form # QC-35

Parameter - SO4_2
Two mg S/L Isotherm Parameter

Batch # ____
Lab Code ____

Submission # __
Run # __
Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used	Samp. Wt. (g)	Initial Soln. Vol. (mL)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg S/L)	Calculated Results (mg S/kg)	SD or % RSD
xx	x.xx	xx.x	xx.xx	xxx.xx	xxx.xxx	xxx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used	Sample Aliq. Vol. (mL)	Vol. Spike Added (mL)	Conc. Spike Added (mg/L)	Aliq. Vol. (mL)	Total Diluted Vol. (mL)	Inst. Reading (mg S/L)	Spike Recovery (%)
xx	xx.xx	xx.xxx	xxxx.x	xx.xx	xxx.xx	xxx.xxx	xxx.xx

QCCS	(mg S/L) xxx.xxx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg S/L) xxx.xxx
True	
High	
Low	
Meas.	

Spike Solution
Inst. Reading (mg S/L) xxx.xxx

Figure B-87. Form QC-35, quality control two mg S/L isotherm parameter.

Form # QC-36

Parameter - SO4 4
Four mg S/L Isotherm Parameter

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysi __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials __

Replicates							
A	B	C	D	E	F	G	H
Samp. # Used xx	Samp. Wt. (g) x.xx	Initial Soln. Vol. (mL) xx.x	Aliq. Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Calculated Results (mg S/kg) xxx.xxx	SD or % RSD xxx.xx

QCCS	(mg S/L) xxx.xxx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg S/L) xxx.xxx
True	
High	
Low	
Meas.	

Spike Solution
Inst. Reading (mg S/L) xxx.xxx

Figure B-88. Form QC-36, quality control four mg S/L isotherm parameter.

Form # QC-37

Parameter - SO4 8
Eight mg S/L Isotherm Parameter

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used xx	Samp. Wt. (g) x.xx	Initial Soln. Vol. (mL) xx.x	Aliq. Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Calculated Results (mg S/kg) xxx.xxx	SD or % RSD xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Aliq. Vol. (mL) xx.xx	Vol. Spike Added (mL) xx.xxx	Conc. Spike Added (mg/L) xxxx.x	Aliq. Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Spike Recovery (%) xxx.xx

QCCS	(mg S/L) xxx.xxx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg S/L) xxx.xxx
True	
High	
Low	
Meas.	

Spike Solution
Inst. Reading (mg S/L) xxx.xxx

Figure B-89. Form QC-37, quality control eight mg S/L isotherm parameter.

Form # QC-38

Parameter - SO4_16
Sixteen mg S/L Isotherm Parameter

Batch # ____
Lab Code ____

Submission # __
Run # __

Re-Analysis __

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used xx	Samp. Wt. (g) x.xx	Initial Soln. Vol. (mL) xx.x	Aliq. Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Calculated Results (mg S/kg) xxx.xxx	SD or % RSD xxx.xx

QCCS	(mg S/L) xxx.xxx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg S/L) xxx.xxx
True	
High	
Low	
Meas.	

Spike Solution
Inst. Reading (mg S/L) xxx.xxx

Figure B-90. Form QC-38, quality control sixteen mg S/L isotherm parameter.

orm # QC-39

Parameter - SO4_32
Thirty-two mg S/L Isotherm Parameter

Batch # ____
Lab Code ____

ubmission # ___
un # ___

e-Analysis ___

Date Analysis Started __/__/__
Date Analysis Completed __/__/__
Date Form Completed __/__/__
Lab Manager Initials ____

Replicates

A	B	C	D	E	F	G	H
Samp. # Used xx	Samp. Wt. (g) x.xx	Initial Soln. Vol. (mL) xx.x	Aliq. Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Calculated Results (mg S/kg) xxx.xxx	SD or % RSD xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. # Used xx	Sample Aliq. Vol. (mL) xx.xx	Vol. Spike Added (mL) xx.xxx	Conc. Spike Added (mg/L) xxxx.x	Aliq. Vol. (mL) xx.xx	Total Diluted Vol. (mL) xxx.xx	Inst. Reading (mg S/L) xxx.xxx	Spike Recovery (%) xxx.xx

QCCS	(mg S/L) xxx.xxx
True	
High	
Low	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(mg S/L) xxx.xxx
True	
High	
Low	
Meas.	

Spike Solution
Inst. Reading (mg S/L) xxx.xxx

Figure B-91. Form QC-39, quality control thirty-two mg S/L isotherm parameter.

Form # 40

Parameter - C_TOT
Total Carbon

Batch # ______
Submission # __
Run # __

Re-Analysis _

Lab Code ______
Date Analysis Started ______
Date Analysis Completed ______
Date Form Completed ______
Lab Manager Initials ___

A	B	C	D	E	F
Samp. #	Sample Wt. (ug) xxxxxx	Factor (counts/ ug-wt%) xx.xxx	Inst. Reading (counts) xxxxxxxxxx	Blk. Inst Reading (counts) xxxxx	Calculated Result (wt %) xx.xxx
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
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42					

Figure B-92. Form 40, total carbon.

Form # 41

Parameter - N_TOT
Total Nitrogen

Batch # ______
Submission # __
Run # __

Re-Analysis _

Lab Code
Date Analysis Started ______
Date Analysis Completed ________
Date Form Completed ________
Lab Manager Initials ____

A	B	C	D	E	F
Samp. #	Sample Wt. (ug) xxxxxx	Factor (counts/ ug-wt%) xx.xxx	Inst. Reading (counts) xxxxxxxxxx	Blk. Inst Reading (counts) xxxxx	Calculated Result (wt %) xx.xxx
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
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37					
38					
39					
40					
41					
42					

Figure B-93. Form 41, total nitrogen.

Form # QC-40

Parameter - C_TOT
Total Carbon

Batch # ______
Submission # __
Run # __

Re-Analysis _

Lab Code ______
Date Analysis Started ________
Date Analysis Completed ________
Date Form Completed ________
Lab Manager Initials ___

Replicate Data

A	B	C	D	E	F	G
Samp. #	Sample Wt. (ug)	Factor (counts/ ug-wt%)	Inst. Reading (counts)	Blk. Inst Reading (counts)	Calculated Result (wt %)	SD or %RSD
	xxxxxx	xx.xxx	xxxxxxxxxx	xxxxx	xx.xxx	xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H	I
Samp. #	Sample Wt. (ug)	Conc. Spike Added (wt %)	Spike Added (ug)	Factor (count/ ug-wt%)	Inst. Reading (counts)	Blank Inst. Reading (count)	Spike plus Sample (wt %)	Spike Recovery (%)
	xxxxxx	xx.xxx	xxxxx	xx.xxx	xxxxxxxxxx	xxxxx	xx.xxx	xxx.xx

QCCS	(wt. %) xx.xxx
True	
Low	
High	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(wt. %) xx.xxx
True	
Low	
High	
Meas.	

Calib. Blank	(wt. %) xx.xxx
CBLK 1	
CBLK 2	
CBLK 3	
CBLK 4	
CBLK 5	
CBLK 6	
CBLK 7	
CBLK 8	

Figure B-94. Form QC-40, quality control total carbon.

Form # QC-41 Parameter - N_TOT
Total Nitrogen

Batch # _____
Submission # __
Run # __

Re-Analysis _

Lab Code _____
Date Analysis Started _______
Date Analysis Completed _______
Date Form Completed _______
Lab Manager Initials ___

Replicate Data

A	B	C	D	E	F	G
Samp. #	Sample Wt. (ug) xxxxxx	Factor (counts ug-wt%) xx.xxx	Inst. Reading (counts) xxxxxxxxxx	Blk. Inst Reading (counts) xxxxx	Calculated Result (wt %) xx.xxx	SD or %RSD xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H	I
Samp. #	Sample Wt. (ug) xxxxxx	Conc. Spike Added (wt %) xx.xxx	Spike Added (ug) xxxxx	Factor (count/ ug-wt%) xx.xxx	Inst. Reading (counts) xxxxxxxxxx	Blank Inst. Reading (count) xxxxx	Spike plus Sample (wt %) xx.xxx	Spike Recovery (%) xxx.xx

QCCS	(wt. %) xx.xxx
True	
Low	
High	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(wt. %) xx.xxx
True	
Low	
High	
Meas.	

Calib. Blank	(wt. %) xx.xxx
CBLK 1	
CBLK 2	
CBLK 3	
CBLK 4	
CBLK 5	
CBLK 6	
CBLK 7	
CBLK 8	

Figure B-95. Form QC-41, quality control total nitrogen.

Form # 42

Parameter - S_TOT
Total Sulfur

Batch # _____
Submission # __
Run # __

Re-Analysis _

Lab Code _____
Date Analysis Started ______
Date Analysis Completed ______
Date Form Completed ______
Lab Manager Initials ___

A	B	C	D	E
Samp. #	Sample Wt. (g) x.xxxx	Inst. Reading (wt %) xx.xxxxx	Blk. Inst. Reading (wt %) xx.xxxxx	Calculated Result (wt %) xx.xxx
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
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41				
42				

Figure B-96. Form 42, total sulfur.

Form # QC-42

Parameter - S_TOT
Total Sulfur

Batch # ______
Submission # __
Run # __

Re-Analysis _

Lab Code
Date Analysis Started ______
Date Analysis Completed ______
Date Form Completed ______
Lab Manager Initials ___

Replicate Data

A	B	C	D	E	F
Samp. #	Sample Wt. (g) x.xxxx	Inst. Reading (wt %) xx.xxxxx	Blk. Inst. Reading (wt %) xx.xxxxx	Calculated Result (wt %) xx.xxx	SD or %RSD xxx.xx

Matrix Spikes

A	B	C	D	E	F	G	H
Samp. #	Sample Wt. (g) x.xxxx	Conc. Spike Added (wt %) xx.xxx	Spike Added (g) xx.xxxx	Inst. Reading (wt %) xx.xxxxx	Blank Inst. Reading (wt %) xx.xxxxx	Spike plus Sample (wt %) xx.xxx	Spike Recovery (%) xxx.xx

QCCS	(wt. %) xx.xxx
True	
Low	
High	
QCCS 1	
QCCS 2	
QCCS 3	
QCCS 4	
QCCS 5	
QCCS 6	
QCCS 7	
QCCS 8	

DL-QCCS	(wt. %) xx.xxx
True	
Low	
High	
Meas.	

Calib. Blank	(wt. %) xx.xxx
CBLK 1	
CBLK 2	
CBLK 3	
CBLK 4	
CBLK 5	
CBLK 6	
CBLK 7	
CBLK 8	

Figure B-97. Form QC-42, quality control total sulfur.

Appendix C
Atomic Absorption Spectroscopy Methods

(Adapted from Section 200.0 in the *Manual of Methods for Chemical Analysis of Water and Wastes* [U.S. Environmental Protection Agency, 1983])

C.1 Overview

Metals in solution may be determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to the determination of aluminum, calcium, iron, potassium, magnesium, and sodium in natural surface waters.

Detection limits, sensitivity, and optimum ranges of the metals will vary with the makes and models of atomic absorption spectrophotometers. The data listed in Table C-1, however, provide some indication of the actual concentration ranges measurable by direct aspiration and by using furnace techniques. In the majority of instances, the concentration range shown in the table by direct aspiration may be extended much lower with scale expansion and conversely extended upwards by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample through solvent extraction techniques. Lower concentrations may also be determined using the furnace techniques. The concentration ranges given in Table C-1 are somewhat dependent on equipment such as the type of spectrophotometer and furnace accessory, the energy source, and the degree of electrical expansion of the output signal. When using furnace techniques, however, the analyst should be cautioned that chemical reactions may occur at elevated temperatures, which may result in either suppression or enhancement of the signal from the element being analyzed. To insure valid data, the analyst should examine each matrix for interference effects (matrix spike analysis), and if detected, should analyze the samples by the method of standard additions.

In direct aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp, which has a cathode made of the element to be determined, is directed through the flame into a monochromator and onto a detector that measures the amount of light absorbed. Absorption depends on the presence of free, unexcited, ground state atoms in the flame. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of atomic absorption spectroscopy.

When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms is vaporized and dissociated for absorption in the tube than in the flame, the use of small sample volumes or detection of low concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption, except a furnace is used to atomize the sample instead of a flame. Radiation from a given excited element is passed through

Table C-1. Atomic Absorption Concentration Ranges[a]

	Flame			Furnace[b,c]	
Metal	Detection Limit (mg/L)	Sensitivity (mg/L)	Optimum Concentration Range (mg/L)	Detection Limit (µg/L)	Optimum Concentration Range (µg/L)
Calcium	0.01	0.08	0.2 to 7	-----	-----
Iron	0.03	0.12	0.3 to 5	1	5 to 100
Magnesium	0.001	0.007	0.02 to 0.5	-----	-----
Potassium	0.01	0.04	0.1 to 2	-----	-----
Sodium	0.002	0.015	0.03 to 1	-----	-----

[a] The concentrations shown are obtainable with any satisfactory atomic absorption spectrophotometer.

[b] For furnace sensitivity values, consult instrument operating manual.

[c] The listed furnace values are those expected when using a 20-µL injection and normal gas flow.

the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor.

The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected specimen to be volatilized. The monochromator isolates the characteristic radiation from the hollow cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

C.1.2 Definitions

1. Optimum concentration range--A range defined by limits expressed in concentration, below which scale expansion should be used and above which curve correction should be considered. This range varies with the sensitivity of the instrument and the operating conditions employed.

2. Sensitivity--The concentration in milligrams of metal per liter that produces an absorption of 1 percent.

3. Dissolved metals--Those constituents (metals) which can pass through a 0.45-µm membrane filter.

4. Suspended metals--Those constituents (metals) which are retained by a 0.45-µm membrane filter.

5. Total metals--The concentration of metals is determined on an unfiltered sample following vigorous digestion.

6. Total recoverable metals--The concentration of metals in an unfiltered sample following treatment with hot, dilute mineral acid.

C.1.3 Interferences

1. Direct Aspiration--The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in the magnesium and calcium determinations. While complexing agents are primarily employed to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

   Chemical interferences may also be eliminated by separating the metal from the interfering material.

   The presence of high dissolved solids in the sample may result in an interference from non-atomic absorbance such as light scattering. If background correction is not available, a non-absorbing wavelength should be checked. Preferably, high solid type samples should be extracted.

   Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess of an easily ionized element.

   Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample, but not being determined, falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multielement lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting, and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

2. Flameless Atomization--Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. It is this effect which should be determined and taken into consideration in the analysis of each different matrix encountered. To verify the absence of matrix or chemical interference, a matrix spike sample is analyzed using the following procedure:

   a. Withdraw two equal aliquots from the sample.

   b. Add a known amount of analyte and dilute both aliquots to the same predetermined volume. The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4 while keeping in mind the optimum concentration range of the analysis. Under no circumstances should the dilution be less than 1:1.

   c. Analyze the diluted aliquots.

d. Multiply the unspiked results by the dilution factor and compare to the original determination.

Agreement of the results (within ±10 percent) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard helps confirm the finding from the dilution analysis. Those samples which indicate the presence of interference should be analyzed by the method of standard additions.

Gases generated in the furnace during atomization may have a molecular absorption band encompassing the analytical wavelength. When this occurs, either the use of background correction or selection of an alternate wavelength outside the absorption band should eliminate this interference. Background correction can also compensate for non-specific broadband absorption interference.

Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care should be taken, however, to prevent loss of the element being analyzed.

Samples containing large amounts of organic materials should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way, broad band absorption will be minimized.

From anion interference studies in the graphite furnace, it is generally accepted that nitric acid is preferable for any digestion of the solubilization step. If another acid in addition to HNO_3 is required, a minimum amount should be used. This applies particularly to hydrochloric and to a lesser extent, to sulfuric and phosphoric acids.

Carbide formation resulting from the chemical environment of the furnace has been observed with certain elements that form carbides at high temperatures. Molybdenum is an example. When this takes place, the metal will be released very slowly from the carbide as atomization continues. For molybdenum, atomization for 30 seconds or more may be required before the signal returns to baseline levels. This problem is greatly reduced, and the sensitivity is increased with the use of prolytically-coated graphite.

C.1.4 Safety

The calibration standards, sample types, and most reagents pose no hazard to the analyst. Protective clothing (laboratory coat and gloves) and safety glasses should be worn when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated hydrochloric acid and ammonium hydroxide solutions should be restricted to a fume hood.

Follow the manufacturer's safety precautions when operating the atomic absorption spectrophotometers. Chain or bolt compressed gas cylinders in an upright position.

C.2 Sample Collection, Preservation, and Storage

For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption, and by (b) depleting concentrations through absorption. Thus, the collection and treatment of the sample prior to analysis requires particular attention. The sample bottle, whether borosilicate glass, polyethylene, polypropylene, or Teflon, should be thoroughly washed with detergent and tap water, should be rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and finally with deionized, distilled water (in that order).

NOTE 1: Chromic acid may be used to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product--NOCHROMIX--available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. (Chromic acid should not be used with plastic bottles.)

NOTE 2: If it can be documented through an active analytical quality control program using spiked samples, reagent blanks and sample blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps might be eliminated from the procedure. Before collection of the sample, a decision must be made as to the type of data desired, i.e., dissolved, suspended, total, or total recoverable. Drinking water samples containing suspended and settleable material should be prepared by using the total recoverable metal procedure.

For the determination of dissolved constituents, the sample must be filtered through a 0.45-µm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus using plain, non-grid marked, membrane filters are recommended to avoid possible contamination.) Use the first 50-100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH of <2. Normally, 3 mL of (1:1) acid per liter should be sufficient to preserve the sample (see Note 3). If hexavalent chromium is to be included in the analytical scheme, a portion of the filtrate should be transferred before acidification to a separate container and should be analyzed as soon as possible. Analyses performed on a sample so treated shall be reported as "dissolved" concentrations.

NOTE 3: If a precipitate is formed upon acidification, the filtrate should be digested. Also, it has been suggested (International Biological Program, Symposium on Analytical Methods, Amsterdam, October 1966) that additional acid, as much as 25 mL of concentrated HCl per liter, may be required to stabilize certain types of highly buffered samples if they are to be stored for any length of time. Therefore, special precautions should be observed for preservation and storage of unusual samples intended for metal analysis.

For the determination of suspended metals a representative volume of unpreserved sample must be filtered through a 0.45-µm membrane filter. When considerable suspended material is present, as little as 100 mL of a well mixed sample is filtered. Record the volume filtered and transfer the membrane filter containing the insoluble material to a 250-mL Griffin beaker and add

3 mL concentrated redistilled HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of concentrated, redistilled HNO_3. Cover and continue heating until the digestion is complete; generally complete digestion is indicated by a light colored residue. Evaporate to near dryness (*do not bake*), add 5 mL distilled HCl (1:1), and warm the beaker gently to dissolve any soluble material. (If the sample is to be analyzed by the furnace procedure, 1 mL of 1:1 distilled HNO_3 per 100 mL dilution should be substituted for the distilled 1:1 HCl.) Wash down the watch glass and beaker walls with deionized, distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected concentrations of metals present. This volume will vary depending on the metal to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended." (See Note 4.)

NOTE 4: Certain metals such as antimony, arsenic, gold, iridium, mercury, osmium, palladium, platinum, rhenium, rhodium, ruthenium, selenium, silver, thallium, tin, and titanium require modification of the digestion procedure, and the individual sheets for these metals should be consulted.

For the determination of total metals the sample is acidified with 1:1 redistilled HNO_3 to a pH of 2 at the time of collection. The sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much suspended material is present, as little as 50-100 mL of well mixed sample will probably be sufficient. (The sample volume required may also vary proportionally with the number of metals to be determined.) Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 mL of concentrated redistilled HNO_3. Place the beaker on a hot plate and evaporate to dryness cautiously, making certain that the sample does not boil. (*do not bake*.) Cool the beaker and add another 3 mL portion of concentrated, redistilled HNO_3. Cover the beaker with a watch glass and return the beaker to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating and add additional acid as necessary until the digestion is complete (generally indicated by a light colored residue or by no change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of redistilled 1:1 HCl (5 mL/100 mL of final solution) and warm the beaker to dissolve any precipitate or residue resulting from evaporation. (If the sample is to be analyzed by the furnace procedure, substitute distilled HNO_3 for 1:1 HCl so that the final dilution contains 0.5% (v/v) HNO_3). Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total." (See Note 4.)

To determine total recoverable metals, acidify the entire sample at the time of collection with concentrated, redistilled HNO_3, 5 mL/L. At the time of analysis, a 100-mL aliquot of well mixed sample is transferred to a beaker or flask. Five mL of distilled HCl (1:1) is added, and the sample is heated on a steam bath or hot plate until the volume has been reduced to 15 to 20 mL; be certain that the samples do not boil. (If the sample is being prepared for furnace analysis, the same process should be followed except HCl should be omitted.) After this treatment the sample is filtered to remove silicates and other insoluble material that could clog the atomizer, and the volume is adjusted to 100 mL. The sample is then ready for analysis. Concentrations so determined shall be reported as "total". (See notes 4, 5, and 6.)

NOTE 5: The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy certain metal complexes if a calorimetric procedure is to be employed for the final determination. When this is suspected, the more vigorous digestion should be used.

NOTE 6: For drinking water analyses by direct aspiration, the final volume may be reduced to effect up to a 10x concentration of the sample if the total dissolved solids in the original sample do not exceed 500 mg/L. The determination is corrected for any nonspecific absorbance, and there is not loss by precipitation.

C.3 Equipment and Supplies

C.3.1 Equipment and Apparatus

1. Atomic absorption spectrophotometer--The required spectrophotometer is a single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip chart recorder.

2. Burner--The burner recommended by the particular instrument manufacturer should be used. For certain elements, a nitrous oxide burner is required.

3. Hollow cathode lamps--Single element lamps are preferred, but multielement lamps may be used. Electrodeless discharge lamps may also be used when available.

4. Graphite furnace--Any furnace device capable of reaching the specified temperatures is satisfactory.

5. Strip chart recorder--A recorder is recommended for furnace work so that there will be a permanent record and so that any problems with the analysis (i.e., drift, incomplete atomization, losses during charring, changes in sensitivity) can be recognized easily.

C.3.2 Reagents and Consumable Materials

General reagents used in each metal determination are listed in this section. Reagents specific to particular metal determinations are listed in the particular procedure description for that metal.

1. Concentrated hydrochloric acid (12M HCl)--Ultrapure grade (Baker Instra-Analyzed or equivalent).

2. HCl (1 percent v/v)--Add 5 mL of concentrated HCl to 495 mL deionized, distilled water.

3. Nitric acid (0.5% v/v) HNO_3--Carefully dilute Ultrapure grade HNO_3 (Baker Instra-Analyzed or equivalent) in deionized, distilled water in the ratio of 0.5 to 100.

4. Stock standard metal solutions--Prepare as directed in the individual metal procedures. Commercially available stock standard solutions may also be used.

5. Dilute calibration standards--Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.

6. Fuel and oxidant--Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

7. Water--Water should meet the specifications for Type I reagent grade water (American Society for Testing and Materials [ASTM], 1984).

C.4 Calibration and Standardization

The calibration procedure varies slightly with the various atomic absorption instruments. For each analyte, calibrate the atomic absorption instrument by analyzing a calibration blank and a series of standards; follow the instructions in the instrument operating manual. The concentration of standards should bracket the expected sample concentration; however, the linear range of the instrument should not be exceeded.

When indicated by the matrix spike analysis, the analytes should be quantified by the method of standard additions. In this method, equal volumes of sample are added to a deionized water blank and to three standards containing different known amounts of the test element. The volume of the blank and of each standard should be the same. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of intersection of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. (See Figure C-1). The method of standard additions can be very useful; however, for the results to be valid, the following limitations should be taken into consideration:

1. The absorbance plot of sample and standards should be linear over the concentration range of concern. For best results, the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20 percent), caution should be exercised.

2. The effect of the interference should not vary as the ratio of analyte to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

3. The determination should be free of spectral interference and corrected for nonspecific background interference.

C.5 Quality Assurance and Quality Control

C.5.1 Precision and Accuracy

1. Determination of Dissolved Calcium--

   In a single laboratory (U.S. Environmental Protection Agency (EPA) Environmental Monitoring Systems Laboratory [EMSL]-Cincinnati) using distilled water spiked at concentrations of 9.0 and 36 mg/L Ca^{2+}, the standard deviations were ±0.3 and ±0.6, respectively. Recoveries at both these levels were 99 percent.

2. Determination of Dissolved Iron--

An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL-Cincinnati. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead, and zinc were added to natural water samples. The statistical results for iron were as follows:

Number of Labs	True Value (μg/L)	Mean Value (μg/L)	Standard Deviation (μg/L)	Accuracy as Percent Bias
82	840	855	173	1.8
85	700	680	178	-2.8
79	438	435	183	-0.7
78	350	348	131	-0.5
57	24	58	69	141
54	10	48	69	382

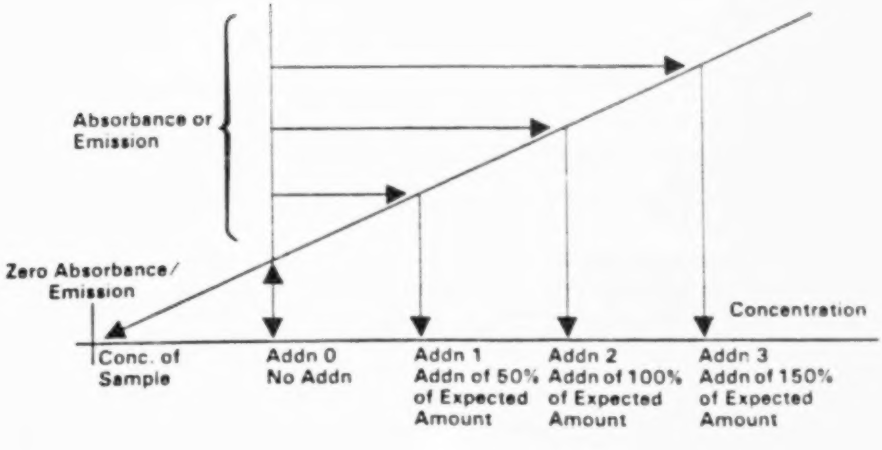
Absorbance or Emission
Zero Absorbance/ Emission
Concentration
Conc. of Sample
Addn 0
No Addn
Addn 1
Addn of 50% of Expected Amount
Addn 2
Addn of 100% of Expected Amount
Addn 3
Addn of 150% of Expected Amount

Figure C-1. Standard additions plot

3. Determination of Dissolved Magnesium--

   In a single laboratory (EMSL-Cincinnati), using distilled water spiked at concentrations of 2.1 and 8.2 mg/L Mg^{2+}, the standard deviations were ±0.1 and ±0.2, respectively. Recoveries at both of these levels were 100 percent.

4. Determination of Dissolved Potassium--

   In a single laboratory (EMSL-Cincinnati), using distilled water samples spiked at concentrations of 1.6 and 6.3 mg/L K^+, the standard deviations were ±0.2 and ±0.5, respectively. Recoveries at these levels were 103 percent and 102 percent, respectively.

5. Determination of Dissolved Sodium--

   In a single laboratory (EMSL-Cincinnati), using distilled water samples spiked at levels of 8.2 and 52 mg/L Na^+, the standard deviations were ±0.1 and ±0.8, respectively. Recoveries at these levels were 102 percent and 100 percent.

C.5.2 Quality Control

Minimum requirements--

1. All quality control data should be maintained and should be available for easy reference or inspection.

2. An unknown performance sample (when available) must be analyzed once per year for the metals measured. Results must be within the control limits established by EPA. If problems arise, they should be corrected, and a follow-up performance sample should be analyzed.

Minimum Daily Control--

1. After a calibration curve composed of a minimum of a reagent blank and three standards has been prepared, subsequent calibration curves must be verified by use of at least a reagent blank and one standard at or near the instrument detection limit (IDL). Daily checks must be within ±10 percent of original curve.

2. If 20 or more samples per day are analyzed, the working standard curve must be verified by running an additional standard at or near the IDL every 20 samples. Checks must be within ±10 percent of the original curve.

Optional Requirements--

1. A current service contract should be in effect on balances and on the atomic absorption spectrophotometer.

2. Class "S" weights should be available to make periodic checks on balances.

3. Chemicals should be dated upon receipt of shipment and replaced as needed or before shelf life has been exceeded.

4. A known reference sample (when available) should be analyzed once per quarter for the metals measured. The measured value should be within the control limits.

5. At least one duplicate sample should be run every 10 samples or with each set of samples to verify precision of the method. Checks should be within the control limits established by EPA.

6. Standard deviations should be obtained and documented for all measurements being conducted.

7. Quality control charts or a tabulation of means and standard deviations should be used to document validity of data on a daily basis.

C.6 Procedure

C.6.1 Flame Atomic Absorption Spectroscopy

Differences among the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for a particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, the lamp should be allowed to warm up for a minimum of 15 minutes unless operated in a double-beam mode.

During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebular flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the element under analysis and calibrate the instrument. Aspirate the samples and determine the concentrations either directly (if the instrument reads directly in concentration units) or from the calibration curve.

C.6.2. Furnace Atomic Absorption Spectroscopy

Furnace devices (flameless atomization) are a useful means of extending detection limits. Because of differences among various makes and models of satisfactory instruments, no detailed operating instructions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of a particular instrument. The following points may be helpful:

1. With flameless atomization, background correction is important, especially below 350 nm. This is because certain samples, when atomized, may absorb or scatter light from the hollow cathode lamp. These effects can be caused by the presence of gaseous molecular species, salt particles, or smoke in a sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high.

2. If all of the analyte is not volatilized during atomization and removed from the furnace, memory effects will occur. This condition depends on several factors (i.e., the volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design). If this situation is detected through blank burns, the

tube should be cleaned by operating the furnace at full power for the required time period at regular intervals in the analytical scheme.

3. Some of the smaller furnace devices, or newer furnaces equipped with feedback temperature control (Instrumentation Laboratories Model 555, Perkin-Elmer Models HGA 220 and HGA 76B, and Barian Model CRA-90) employing faster rates of atomization, can be operated using lower atomization temperatures for shorter time periods than those listed in this method.

4. In many cases, prior digestion of the sample is not required if a representative aliquot of sample can be pipetted into the furnace. However, prior digestion provides a more uniform matrix and possibly lessens matrix effects.

5. Inject a measured microliter aliquot of the sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and can help detect furnace pipetting errors.

C.6.3 Procedure for Determination of Dissolved Calcium

Samples for determination of dissolved calcium are analyzed by flame atomic absorption spectroscopy for calcium (U.S. EPA, 1983).

1. Preparation of lanthanum chloride matrix modifier solution ($LaCl_3$)--Dissolve 29 g of La_2O_3, slowly and in small portions, in 250 mL of concentrated HCl (*Caution:* reaction is violent) and dilute to 500 mL with deionized, distilled water.

2. Preparation of calcium standard solutions--

   a. Calcium stock solution (500 mg/L Ca^{2+})--Suspend 1.250 g of $CaCO_3$ (analytical reagent grade, dried at 180 °C for 1 hour before weighing in water and dissolved cautiously with a minimum of dilute HCl). Dilute to 1,000 mL with deionized, distilled water.

   b. Dilute calibration standards--Each day, quantitatively prepare a series of dilute Ca^{2+} standards from the calcium stock solution to span the desired concentration range.

3. Suggested Instrumental Conditions (General)--

   a. Lamp--Ca^{2+}, hollow cathode.

   b. Wavelength--422.7 nm.

NOTE: The 239.9 nm line may also be used. This line has a relative sensitivity of 120.

   c. Fuel--acetylene.

   d. Oxidant--air.

   e. Flame--reducing.

4. Analysis Procedure--

   a. To each 10.0-mL volume of dilute calibration standard, blank, and sample add 1.00 mL of $LaCl_3$ solution (e.g., add 2.0 mL of $LaCl_3$ solution to 20.0 mL of sample).

   b. Calibrate the instrument as directed by the manufacturer.

   c. Analyze the samples, including quality control (QC) samples.

   d. Dilute and reanalyze any samples with a concentration exceeding the calibrated range.

   e. Report results as mg/L Ca^{2+}.

NOTE 1: Phosphate, sulfate, and aluminum interfere but are masked by the addition of lanthanum. Because low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute acid solution. Concentrations of magnesium greater than 1,000 mg/L also cause low calcium values. Concentrations of up to 500 mg/L each of sodium, potassium, and nitrate cause no interference.

NOTE 2: Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.

NOTE 3: The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame.

C.6.4 Procedure for Determination of Dissolved Iron

The samples for determination of dissolved iron are analyzed by flame atomic absorption spectroscopy (U.S. EPA, 1983).

1. Preparation of iron standard solutions--

   a. Iron stock solution (1,000 mg/L Fe^{3+})--Carefully weigh 1.000 g of pure iron wire (analytical reagent grade) and dissolve in 5 mL of concentrated HNO_3, warming if necessary. When iron is completely dissolved, bring the volume of the solution to 1 L with deionized, distilled water.

   b. Dilute calibration standards--Each day, quantitatively prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent (v/v) HNO_3).

2. Suggested Instrumental Conditions (General)--

   a. Lamp--Fe^{3+}, hollow cathode.

   b. Wavelength--248.3 nm.

NOTE: The following lines may also be used: 248.8 nm, relative sensitivity 2; 271.9 nm, relative sensitivity 4; 302.1 nm, relative sensitivity 5; 252.7 nm, relative sensitivity 6; 372.0 nm, relative sensitivity 10.

c. Fuel--acetylene.

d. Oxidant--air.

e. Flame--oxidizing.

3. Analysis Procedure--

a. Calibrate the instrument as directed by the instrument manufacturer.

b. Analyze the samples.

c. Dilute and reanalyze any samples with a concentration exceeding the calibrated range.

d. Report results in mg/L Fe^{3+}.

C.6.5 Procedure for Determination of Dissolved Magnesium

The samples for determination of dissolved magnesium are analyzed by flame atomic absorption spectroscopy.

1. Preparation of lanthanum chloride matrix modifier solution ($LaCl_3$)--Dissolve 29 g of La_2O_3, slowly and in small portions, in 250 mL concentrated HCl (*Caution:* reaction is violent), and dilute to 500 mL with deionized, distilled water.

2. Preparation of magnesium standard solutions--

   a. Stock solution (500 mg/L Mg)--Dissolve 0.829 g of magnesium oxide (MgO, analytical reagent grade) in 10 mL of HNO_3 and dilute in 1 L with water.

   b. Dilute calibration standards--Each day, quantitively prepare from the Mg stock solution a series of Mg^{2+} standards that span the desired concentration range.

3. Suggested Instrumental Conditions (General)--

   a. Lamp--Mg^{2+}, hollow cathode.

   b. Wavelength--285.2 nm.

NOTE: The line at 202.5 nm may also be used. This line has a relative sensitivity of 25.

   c. Fuel--acetylene.

   d. Oxidant--air.

   e. Flame--oxidizing.

4. Analysis Procedure--

   a. To each 10.0 mL of dilute calibration standard, blank, and sample, add 1.00-mL of $LaCl_3$ solution (e.g., add 2.0 mL $LaCl_3$ solution to 20.0 mL of sample).

   b. Calibrate the instrument as directed by the manufacturer.

   c. Analyze the samples.

   d. Dilute and reanalyze any samples with a concentration exceeding the linear range.

   e. Report results as mg/L Mg^{2+}.

NOTE 1: The interference caused by aluminum at concentrations greater than 2 mg/L is masked by additional lanthanum. Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/L.

NOTE 2: To cover the range of magnesium values normally observed in surface waters (0.1 to 20 mg/L), it is suggested that either the 202.5-nm line be used or that the burner head be rotated. A 90° rotation of the burner head will produce approximately one-eighth the normal sensitivity.

C.6.6 Procedure for Determination of Dissolved Potassium

The samples for determination of dissolved potassium are analyzed by flame atomic absorption spectroscopy (U.S. EPA 1983).

1. Preparation of potassium standard solutions--

   a. Potassium stock solution (100 mg/L K^+)--Dissolve 0.1907 g of KCl (analytical reagent grade, dried at 110 °C) in deionized, distilled water and bring the volume of the solution to 1 L.

   b. Dilute calibration standards--Each day, quantitatively prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent (v/v) HNO_3).

2. Suggested Instrumental Conditions (General)--

   a. Lamp--K^+, hollow cathode.

   b. Wavelength--766.5.

NOTE: The line at 404.4 nm may also be used. This line has a relative sensitivity of 500.

   c. Fuel--acetylene.

   d. Oxidant--air.

   e. Flame--slightly oxidizing.

3. Analysis Procedure--

   a. Calibrate the instrument as directed by the manufacturer.

   b. Analyze the samples.

   c. Dilute and reanalyze any samples with a concentration exceeding the calibrated range.

   d. Report results as mg/L K^+.

NOTE 1: In air-acetylene or other high-temperature flames (greater than 2,800 °C), potassium can experience partial ionization which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization suppressive effect and thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na^+ to K^+ is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1,000 μg/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks should be analyzed to correct for potassium impurities in the buffer stock.

NOTE 2: To cover the range of potassium values normally observed in surface waters (0.1 to 20 mg/L), it is suggested that the burner head be rotated. A 90° rotation of the burner head provides approximately one-eighth the normal sensitivity.

C.6.7 Procedure for Determination of Dissolved Sodium

The samples for determination of dissolved sodium are analyzed by flame atomic absorption spectroscopy for sodium (U.S. EPA, 1983).

1. Preparation of sodium standard solutions--

   a. Sodium stock solution (1,000 mg/L Na^+)--Dissolve 2.542 g of NaCl (analytical reagent grade, dried at 140 °C) in deionized, distilled water and bring the volume of the solution to 1 L.

   b. Dilute calibration standards--Each day, quantitatively prepare a series of calibration standards spanning the desired concentration range. Match the acid content of the standards to that of the samples (ca. 0.1 percent (v/v) HNO_3).

2. Suggested Instrumental Conditions (General)--

   a. Lamp--Na^+, hollow cathode.

   b. Wavelength--589.6 nm.

NOTE: The 330.2 nm resonance line of sodium, which has a relative sensitivity of 185, provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.

   c. Fuel--acetylene.

d. Oxidant--air.

e. Flame--oxidizing.

3. Analysis Procedure--

a. Calibrate the instrument as directed by the manufacturer.

b. Analyze the samples.

c. Dilute and reanalyze any samples with a concentration exceeding the calibrated range.

d. Report results as mg/L Na^+.

NOTE: Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1000 mg/L) to both standards and samples.

C.6.8 Direct Aspiration

Generally, instruments are calibrated to give sample results directly in concentration units. For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorption of 0 to 80 percent. The correct method is to convert the percent absorption readings to absorbance and to plot that value against concentration. The following relationship is used to convert absorption values to absorbance:

$$\text{absorbance} = \log(100 \div \%T) = 2 - \log \% T$$

where: $\% T = 100 - \%$ absorption

As the curves are frequently nonlinear, especially at high absorption values, the number of standards should be increased in that portion of the curve.

1. Direct determination of liquid samples: Read the metal value in mg/L from the calibration curve or directly from the readout system of the instrument. If dilution of sample was required:

$$\text{mg/L metal in sample} = A\,[(C + B) \div C]$$

where: A = mg/L of metal in diluted aliquot from calibration curve
B = mL of deionized, distilled water used for dilution
C = mL of sample aliquot

2. For samples containing particulates:

$$\text{mg/L metal in sample} = A\,(V \div C)$$

where: A = mg/L of metal in processed sample from calibration curve
V = final volume of the processed sample in mL
C = mL of sample aliquot processed

3. For solid sample: report all concentrations as mg/kg dry weight:

$$\text{mg metal/kg sample} = (A \times V) \div D$$

where: A = mg/L of metal in processed sample from calibration curve
V = final volume of the processed sample in mL
D = weight of wet sample in grams

C.6.9 Furnace Calculations

For determination of metal concentration by the furnace method. Read the metal value in µg/L from the calibration curve or directly from the readout system of the instrument.

1. If different size furnace injection volumes are used for samples than for standards:

$$\mu\text{g/L of metal in sample} = Z\ (S \div U)$$

where: Z = µg/L of metal from calibration curve or readout system
S = µL volume standard injected into furnace for calibration curve
U = µL volume of sample injected for analysis

2. If dilution of sample was required, and if sample injection volume is the same as for the standard:

$$\mu\text{g/L of metal in sample} = Z\ [(C + B) \div C]$$

where: Z = µg/L metal in diluted aliquot from calibration curve
B = mL of deionized, distilled water used for dilution
C = mL of sample aliquot

3. For samples containing particulates:

$$\mu\text{g/L of metal in sample} = Z\ (V \div C)$$

where: Z = µg/L of metal in processed sample from calibration curve
V = final volume of processed sample in mL
C = mL of sample aliquot processed

4. For solid samples: Report all concentrations as mg/kg dry weight.

4a. Dry sample:

$$\text{mg metal/kg sample} = (Z \times V) \div 1{,}000D$$

where: Z = µg/L of metal in processed sample from calibration curve
V = final volume of processed sample in mL
D = weight of dry sample in grams

4b. Wet sample:

$$\text{mg metal/kg sample} = (Z \times V) + (W \times P \times 1{,}000)$$

where: Z = µg/L of metal in processed sample from calibration curve
V = final volume of processed sample in mL
W = weight of dry sample in grams
P = % solids

C.7 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water,* D 1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

U.S. Environmental Protection Agency. 1983 (revised). *Methods for Chemical Analysis of Water and Wastes.* EPA 600/4-79-020. U.S. Environmental Protection Agency, Cincinnati, Ohio.

Appendix D

Inductively Coupled Plasma Atomic Emission Spectrometric Method for Trace Element Analyses of Water and Wastes

(Adapted from Method 200.7 in the *Manual for Chemical Analysis of Water and Wastes*
[U.S. Environmental Protection Agency, 1983])

D.1 Overview

This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial waste waters. Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1,500 mg/L. Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects.

Table D-1 lists the recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization for the specific elements analyzed by inductively coupled argon plasma (ICP) in the Direct/Delayed Response Project (DDRP) (see sections 12, 13, 14, and 16). Actual working detection limits are sample-dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available, and as required.

Table D-1. Recommended Wavelengths and Estimated Instrumental Detection Limits

Element	Wavelength (nm)[a]	Estimated detection limit (μg/L)[b]
Aluminum	308.215	45
Calcium	317.933	10
Iron	259.940	7
Magnesium	279.079	30
Silicon	288.158	58

[a] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

[b] The estimated instrumental detection limits as shown are taken from Fassel (1982). They are given as a guide for an instrumental limit. The actual method detection limits are sample-dependent and may vary as the sample matrix varies.

Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

D.1.1 Summary of Method

The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic transported by an argon carrier stream to an ICP, which is produced by a radio frequency (RF) generator. In the plasma (which is at a temperature of 6,000 to 10,000 °K), the analytes in the aerosol are atomized, ionized, and ionic emission spectra is produced. The spectra from all analytes are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed by a computer system. The signal is proportional to the analyte concentration and is calibrated by analyzing a series of standards (U.S. Environmental Protection Agency [EPA], 1983; Fassel, 1982).

A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background should be measured adjacent to analyte lines during sample analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, is determined by the complexity of the spectrum adjacent to the analyte line. The position used should be free of spectral interference and should reflect the same change in background intensity as occurs at the analyte wavelength measured. Generally, each instrument has different background handling capabilities. The instrument operating manual should be consulted for guidance.

The possibility of additional interferences should also be recognized, and appropriate corrections should be made.

D.1.2 Definitions

1. Dissolved -- Those elements which will pass through a 0.45-μm membrane filter.

2. Suspended -- Those elements which are retained by a 0.45-μm membrane filter.

3. Total -- The concentration determined on an unfiltered sample following vigorous digestion, or the sum of the dissolved plus suspended concentrations.

4. Total recoverable -- The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

5. Instrumental detection limit -- The concentration equivalent to a signal due to the analyte and which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

6. Sensitivity -- The slope of the analytical curve (i.e., functional relationship between emission intensity and concentration).

7. Instrument check standard -- A multielement standard of known concentration prepared by the analyst to monitor and verify instrument performance on a daily basis.

8. Interference check sample -- A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors.

9. Quality control sample -- A solution obtained from an outside source having known concentration values; used to verify the calibration standards.

10. Calibration standards -- A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

10. Calibration standards -- A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

11. Linear dynamic range -- The concentration range over which the analytical curve remains linear.

12. Reagent blank -- A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme.

13. Calibration blank -- A volume of deionized, distilled water acidified with HNO_3 and HCl.

14. Method of standard additions -- The standard additions technique involves the use of the unknown and the unknown plus a known amount of standard.

D.1.3 Interferences

The following types of interference effects may contribute to inaccuracies in the determination of trace elements:

1. Spectral Interferences--Spectral interferences can be categorized as (a) overlap of a spectral line from another element, (b) unresolved overlap of molecular band spectra, (c) background contribution from continuous or recombination phenomena, and (d) background contribution from stray light from the line emission of high-concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data which requires the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multielement instrumentation should assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Table D-2 lists some interference effects for the recommended wavelengths given in Table D-1. The interference information is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interfering element. The values in the table are only approximate and should be used as a guide for determining potential interferences. Actual values should be determined for each analytical system when necessary.

Table D-2. Analyte Concentration Equivalents (mg/L) Arising from Interferences at the 100-mg/L Level

		Interference										
Analyte	Wavelength[a] (nm)	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V	
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	--	
Calcium	317.933		--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--	
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12	
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01	
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--	

[a] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be be sustituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

Only those interferents listed were investigated. The blank spaces in Table D-2 indicate that measurable interferences were not observed for the interferant concentrations listed in Table D-3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2 to 5 percent of the peaks generated by the analyte concentrations (also listed in Table D-3).

2. Physical Interferences--Physical interferences generally are considered to be effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples that contain high dissolved solids or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they can be reduced by dilution of the sample or utilization of standard additions techniques.

   High dissolved solids may also cause salt buildup at the tip of the nebulizer. This affects aerosol flow rate, causing instrumental drift. Wetting the argon prior to nebulization, using a tip washer, or diluting the sample can be used to control this problem. Better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

Table D-3. Interferant and Analyte Elemental Concentrations Used for Interference Measurements In Table D-2

Analytes	Concentration (mg/L)	Interferents	Concentration (mg/L)
Al	10	Al	1,000
Ca	1	Ca	1,000
Fe	1	Cr	200
Mg	1	Cu	200
Na	10	Fe	1,000
Si	1	Mg	1,000
		Nn	200
		Ni	200
		Ti	200
		V	200

3. Chemical Interferences--Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are negligible with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (i.e., incident power, observation position), by buffering of the sample, matrix matching, and standard addition procedures. These types of interferences can be dependent on matrix type and the specific analyte element.

D.1.4 Interference Tests

Whenever a new or unusual sample matrix is encountered, a series of tests should be performed prior to reporting concentration data for analyte elements. These tests, outlined below, ensure that neither positive nor negative interference effects are operative on any of the analyte elements, thereby distorting the accuracy of the reported values.

1. Serial Dilution--If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 percent of the original determination (or within some acceptable control limit that has been established for that matrix). If it does not, a chemical or physical interference effect should be suspected.

2. Spiked Addition--The recovery of a spiked addition added at a minimum level of 10× the instrumental detection limit (maximum 100×) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard additions analysis procedure can usually compensate for this effect.

   Caution: The standard addition technique does not detect coincidental spectral overlap. If overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

3. Comparison with alternate method of analysis--When investigating a new sample matrix, a comparison test may be performed with other analytical techniques, such as atomic absorption spectrometry or other approved methodology.

4. Wavelength scanning of analyte line region--If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

D.1.5 Safety

The toxicity or carcinogenicity of each reagent used in this method has not been defined precisely. Each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals should be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data safety sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (Department of Health, Education, and Welfare [DHEW], 1977; OSHA, 1976; American Chemical Society [ACS], 1979) for the information of the analyst.

D.2 Sample Collection, Preservation, and Storage

For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1:1) nitric acid, tap water, (1:1) hydrochloric acid, tap water, and finally deionized, distilled water (in that order).

NOTE 1: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. Chromic acid should not be used with plastic bottles.

NOTE 2: If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

Before collection of the sample, a decision must be made as to the type of data desired (i.e., dissolved, suspended, or total) so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

For the determination of dissolved elements, the sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50 to 100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1:1) HNO_3 to a pH of 2 or less. Normally, 3 mL of (1:1) acid per liter should be sufficient to preserve a sample.

For the determination of suspended elements, a measured volume of unpreserved sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and shipment. No preservative is required.

For the determination of total or total recoverable elements, the sample is acidified with (1:1) HNO_3 to pH 2 or less as soon as possible, preferably at the time of collection. The sample is not filtered before processing.

D.3 Equipment and Supplies

D.3.1 Inductively Coupled Plasma Atomic Emission Spectrometer

1. Computer-controlled atomic emission spectrometer with background correction.

2. Radio frequency generator.

3. Argon gas supply, welding grade or better.

D.3.2 Reagents

Acids used in the preparation of standards and for sample processing must be ultra-high purity spectroscopic grade or equivalent. Redistilled acids are acceptable.

Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for 1 hour at 105 °C unless otherwise specified. Typical stock solution preparation procedures for the elements typically analyzed in soil samples are described in steps 7 through 12, below. A mixed calibration standard solution may be prepared by combining appropriate volumes of the stock solutions in volumetric flasks. Add 2 mL of (1:1) HNO_3 and 10 mL of (1:1) HCl and dilute to 100 mL with deionized, distilled water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP-fluorocarbon or unused polyethylene bottle for storage. Freshly mixed standards should be prepared as needed with the realization that concentration can change due to aging. Calibration standards must be verified initially by using a quality control sample and should be monitored weekly for stability.

Caution: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

In addition to the calibration standards, blank samples, an instrument check standard, an interference check sample, and a quality control sample are also required for the analyses. Blanks are described in steps 13 and 14; the remaining quality control samples are described in steps 15 through 17.

1. Acetic acid, concentrated (sp. gr. 1.06).

2. Hydrochloric acid, concentrated (sp. gr. 1.19).

3. Hydrochloric acid, (1:1)--Add 500 mL concentrated HCl (sp. gr. 1.19) to 400 mL deionized, distilled water and dilute to 1 liter.

4. Nitric acid, concentrated (sp. gr. 1.41).

5. Nitric acid, (1:1)--Add 500 mL concentrated HNO_3 (sp. gr. 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.

6. Deionized, distilled water--Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards, and as dilution water. The purity of this water must be equivalent to American Society for Testing and Materials (ASTM) Type II reagent water of Specification D-1193-77 (ASTM 1984).

7. Aluminum solution, stock, 1 mL = 100 μg Al^{3+}--Dissolve 0.100 g of aluminum metal in an acid mixture of 4 mL of (1:1) HCl and 1 mL of concentrated HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a 1-L volumetric flask, add an additional 10 mL of (1:1) HCl, and dilute to 1000 mL with deionized, distilled water.

8. Calcium solution, stock, 1 mL = 100 μg Ca^{2+}--Suspend 0.2498 g $CaCO_3$, dried at 180 °C for 1 hour before weighing, in deionized, distilled water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

9. Iron solution, stock, 1 mL = 100 μg Fe^{3+}--Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5 mL of concentrated HNO_3, and dilute to 1000 mL with deionized, distilled water.

10. Magnesium solution, stock, 1 mL = 100 μg Mg^{2+}--Dissolve 0.1658 g MgO in a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

11. Silica solution, stock, 1 mL = 100 μg SiO_2--Do not dry. Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in deionized, distilled water. Add 10.0 mL concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

12. Sodium solution, stock, 1 mL = 100 μg Na^+--Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

13. Calibration blanks--Dilute 2 mL of (1:1) HNO_3 and 10 mL of (1:1) HCl to 100 mL with deionized, distilled water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

14. Reagent blanks--Reagent blanks contain all the reagents in the same volumes as used in the processing of the samples. The reagent blank should be carried through the complete procedure and should contain the same acid concentration in the final solution as in the sample solution used for analysis.

15. Instrument check standard--Combine compatible elements at a concentration equivalent to the midpoint of their respective calibration curves.

16. Interference check sample--Select a representative sample which contains minimal concentrations of the analytes of interest but a known concentration of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 μg/L or 5 times the estimated detection limits given in Table D-1. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed is varied, a synthetically prepared sample may be used as long as the above criteria and intent are met.

17. Quality control sample--Prepare a solution in the same acid matrix as the calibration standards at a concentration near 1 mg/L.

D.4 Preparation

D.4.1 Sample Preparation

For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. If a precipitate has formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid or by heat, or both.

For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 150-mL Griffin beaker and add 4 mL concentrated HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of concentrated HNO_3. Cover and continue heating until the digestion is complete; digestion is generally indicated by a light colored digestate. Evaporate to near dryness (2 mL), cool, add 10 mL HCl (1:1) and 15 mL deionized, distilled water per 100 mL dilution, and warm the beaker gently for 15 minutes to dissolve any precipitate or residue. Allow to cool, wash down the watch glass and beaker walls with deionized distilled water, and filter the sample to remove any insoluble material that could clog the nebulizer. Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended."

> NOTE: In place of filtering, and after diluting and mixing, the sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

For the determination of total elements, choose a measured volume of the well mixed, acid-preserved sample appropriate for the expected level of elements and transfer it to a Griffin beaker. Add 3 mL of concentrated HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area on the bottom of the beaker is allowed to go dry. Cool the beaker and add another 5 mL portion of concentrated HNO_3. Cover the beaker with a watch glass and return it to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness and cool the beaker. Add 10 mL of (1:1) HCl and 15 mL of deionized, distilled water per 100 mL of final solution and warm the beaker gently for 15 minutes to dissolve any precipitate or residue resulting from evaporation. Allow to cool; wash down the beaker walls and watch glass with deionized, distilled water and filter the sample to remove insoluble material that could clog the nebulizer. Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

> NOTE: If the sample analysis solution has a different acid concentration from that given below, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

For the determination of total recoverable elements, choose a measured volume of a well mixed, acid-preserved sample appropriate for the expected level of elements and transfer it to a Griffin beaker. Add 2 mL of (1:1) HNO_3 and 10 mL of (1:1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL, making certain the sample does not boil. After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer. Adjust the volume to 100 mL and mix. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

D.4.2 Calibration and Standardization

Prepare and calibrate blank standards and a series of dilute calibration standards from the stock solution spanning the expected sample concentration range. Match the acid content of the standards to that of the samples. A multielement standard may be prepared.

D.4.3 Operating Conditions

Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the analytical requirements, and to maintain quality control data confirming instrument performance and analytical results.

D.5 Quality Assurance and Quality Control

D.5.1 Instrument Quality Control Checks

Check the instrument standardization by analyzing appropriate quality control check standards as indicated below:

1. Analyze an appropriate instrument check standard containing the elements of interest at a frequency of 10 percent. This check standard is used to determine instrumental drift. If agreement is not within 5 percent of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated. Analyze the calibration blank at a frequency of 10 percent. The result should be within the established control limits of 2 standard deviations of the mean value. If not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem, and recalibrate the instrument.

2. To verify interelement and background correction factors, analyze the interference check sample at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control limits of 1.5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem, and recalibrate the instrument.

3. A quality control sample obtained from an outside source must first be used for the initial verification of the calibration standards. A fresh dilution of this sample must be analyzed every week thereafter to monitor the instrument stability. If the results are not within ±5 percent of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

D.5.2 Precision and Accuracy

In an EPA round-robin phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table D-4 lists the true value, the mean reported value, and the mean percent relative standard deviation.

Table D-4. Inductively Coupled Plasma Emission Spectroscopy Precision and Accuracy Data[a]

	Sample 1			Sample 2			Sample 3		
Element	True Value (μg/L)	Mean Reported Value (μg/L)	Mean %RSD[b]	True Value (μg/L)	Mean Reported Value (μg/L)	Mean %RSD	True Value (μg/L)	Mean Reported Value (μg/L)	Mean %RSD
Al	700	696	5.6	60	62	33	160	161	13.0
Fe	600	594	3.0	20	19	15	180	178	6.0

[a] Not all elements were analyzed by all laboratories. Ca and Mg were not determined.
[b] %RSD = percent relative standard deviation.

D.6 Procedure

1. Set up instrument with proper operating parameters as established in Section D.4.3. The instrument must be allowed to become thermally stable before analysis begins. This usually requires at least 30 minutes of operation prior to calibration.

2. Initiate appropriate operating configuration of computer.

3. Profile and calibrate instrument according to recommended procedures described in Section D.4.2, using the typical mixed calibration standard solutions described in Section D.3.2. Flush the system with the calibration blank between each standard. (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

4. Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ±5 percent (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

5. Begin the sample run, flushing the system with the calibration blank solution between each sample. Analyze the instrument check standard and the calibration blank after each 10 samples.

6. If it has been found that methods of standard additions are required, the following procedure is recommended:

   The standard additions technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal and thus produces a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

   $$c_x = \frac{S_B V_S c_S}{(S_A - S_B)\, V_x}$$

   Where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x, and thus c_s is much greater than c_x. If a concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

   a. The analytical curve must be linear.

b. The chemical form of the analyte added must respond in the same manner as the analyte in the sample.

c. The interference effect must be constant over the working range of concern.

d. The signal must be corrected for any additive interference.

D.7 Calculations

Generally, instruments are calibrated to output sample results directly in concentration units. If not, then a manual calibration curve should be prepared and sample concentrations determined by comparing the sample signal to the calibrated curve. If dilutions were performed, the appropriate factor should be applied to sample values. Report results as mg/L for each analyte.

D.8 References

American Chemical Society. 1979. *Safety in Academic Laboratories,* 3rd ed. Committee on Chemical Safety, ACS, Washington, D.C.

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water,* D-1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

Department of Health, Education, and Welfare. 1977. *Carcinogens - Working with Carcinogens.* No. 77-206. DHEW, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, Ohio.

Fassel, V. A. 1982. *Analytical Spectroscopy with Inductively Coupled Plasma - Present Status and Future Prospects.* In: Recent Advances in Analytical Spectroscopy. Pergamon Press, Oxford and New York.

Occupational Safety and Health Administration. 1976. *OSHA Safety and Health Standards, General Industry.* OSHA 2206 (29 CFR 1910). OSHA, Washington, D.C.

U.S. Environmental Protection Agency. 1983 (revised). *Methods for Chemical Analysis of Water and Wastes.* EPA-600/4-79-020. U.S. Environmental Protection Agency, Cincinnati, Ohio.

Appendix E

Emission Spectroscopic Methods

(Adapted from Methods 324B and 322B in *Standard Methods for the Examination of Water and Wastewater* [APHA, 1985])

E.1 Overview

When analyzing by emission spectroscopy (ES), the better instruments can be used to determine sodium levels approximating 100 μg/L. With proper modifications in technique, the range of sodium measurement can be extended to 10 μg/L or lower. Potassium levels of approximately 0.1 mg/L can also be determined.

E.1.1 Summary of Method

Trace amounts of sodium and potassium are determined by ES at wavelengths of 589 and 766.5 nm, respectively. The sample is sprayed into a gas flame, and excitation is carried out under carefully controlled and reproducible conditions. The desired spectral line is isolated by the use of interference filters or by a suitable slit arrangement in light dispersing devices such as prisms or gratings. The intensity of light is measured by a phototube potentiometer or other appropriate circuit. The intensity of light at the appropriate wavelength (e.g., 589 nm for Na^+) is approximately proportional to the concentration of the element. If alignment of the wavelength dial with the prism is not precise in the available photometer, the exact wavelength setting can be determined from the maximum needle deflection and can then be used for the emission measurements. The calibration curve may be linear, but has a tendency to level off at higher concentrations.

E.1.2 Interferences

Emission spectrometers operating on the internal standard principle may require adding a standard lithium solution to each working standard and sample. The optimum lithium concentration may vary among individual instruments; minimize interference by the following:

1. Operate in the lowest practical range.

2. Add radiation buffers to suppress ionization and anion interference. Among common anions capable of causing radiation interference are Cl^-, SO_4^{2-}, and HCO_3^- in relatively large amounts.

3. Introduce identical amounts of the same interfering substances present in the sample into the calibration standards.

4. Prepare a family of calibration curves encompassing incremental concentrations of a common interferant.

5. Apply an experimentally determined correction in those instances where the sample contains a single important interference.

6. Remove interfering ions.

7. Remove burner clogging particulate matter from the sample by filtering through a quantitative filter paper of medium retentiveness.

8. Incorporate a nonionic detergent in the standard lithium solution to assure proper aspirator function.

9. Use the standard additions technique. The standard additions approach is described in Section C.4. Its use involves adding an identical portion of sample to each standard and determining the sample concentration by mathematical or graphical evaluation of the calibration data.

10. Use the internal standard technique. Potassium and calcium interfere with sodium determination by the internal-standard method if the potassium-to-sodium ratio is ≥5:1 and the calcium-to-sodium ratio is ≥10:1. Sodium and calcium may interfere with potassium determination by the internal standard method if the sodium-to-potassium ratio is ≥5:1 or the calcium-to-potassium ratio is ≥10:1. Magnesium interference does not appear until the magnesium-to-sodium ratio or magnesium-to-potassium ratio exceeds 100 percent.

E.1.3 Safety

Wear protective clothing (laboratory coat and gloves) and safety glasses when preparing reagents, especially when concentrated acids and bases are used. The use of concentrated acids should be restricted to a fume hood. Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

Follow the safety precautions of the manufacturer when operating instruments. Gas cylinders should always be chained or bolted in an upright position.

E.2 Sample Collection, Preservation, and Storage

For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents, and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1:1) nitric acid, tap water, (1:1) hydrochloric acid, tap water and finally deionized, distilled water (in that order).

E.3 Equipment and Supplies

E.3.1 Equipment Specifications

1. Emission spectrometer, direct-reading or internal-standard type; or an atomic absorption spectrometer operated in the flame emission mode.

E.3.2 Reagents

NOTE 1: Rinse all glassware with 1:15 HNO_3 followed by several portions of DI water.

NOTE 2: To minimize sodium or potassium pickup, store all solutions in plastic bottles. Use small containers to reduce the amount of dry element that may be picked up from the bottle walls when the solution is poured. Shake each container thoroughly to wash accumulated salts from walls before pouring solution.

1. Standard lithium solution--Use either LiCl or $LiNO_3$ to prepare standard lithium solution containing 1.00 mg Li/1.00 mL.

   a. Dry LiCl overnight in an oven at 105 °C. Weigh rapidly 6.109 g, dissolve in water, and dilute to 1,000 mL.

   b. Dry $LiNO_3$ overnight in an oven at 105 °C. Weigh rapidly 9.935 g, dissolve in water, and dilute to 1,000 mL.

   Prepare a new calibration curve whenever the standard lithium solution is changed. Where circumstances warrant, alternatively prepare a standard lithium solution containing 2.00 mg or even 5.00 mg Li/1.00 mL.

2. Stock sodium solution--Dissolve 2.542 g NaCl dried at 140 °C and dilute to 1000 mL with water; 1.00 mL = mg Na^+.

3. Intermediate sodium solution--Dilute 10.00 mL stock sodium solution with water to 100.0 mL; 1.00 mL = 100 μg Na^+. Use this intermediate solution to prepare calibration curve in sodium range of 1 to 10 mg/L.

4. Standard sodium solution--Dilute 10.00 mL intermediate sodium solution with water to 100 mL; 1.00 mL = 10.0 μg Na^+. Use this solution to prepare calibration curve in sodium range of 0.1 to 1.0 mg/L.

5. Stock potassium solution--Dissolve 1.907 g KCl dried at 110 °C and dilute to 1000 mL with water; 1 mL = 1.00 mg K^+.

6. Intermediate potassium solution--Dilute 10.0 mL stock potassium solution with water to 100 mL; 1.00 mL = 0.100 mg K^+. Use this solution to prepare calibration curve in potassium range of 1 to 10 mg/L.

7. Standard potassium solution--Dilute 10.0 mL intermediate potassium solution with water to 100 mL; 1.00 mL = 0.010 mg K^+. Use this solution to prepare calibration curve in potassium range of 0.1 to 1.0 mg/L.

8. Water--Water used in all preparations should conform to ASTM specifications for Type I reagent grade water (ASTM, 1984).

E.4 Calibration and Standardization

NOTE: Locate instrument in an area away from direct sunlight or constant light emitted by an overhead fixture and free of drafts, dust, and tobacco smoke. Guard against contamination from corks, filter paper, perspiration, soap, cleansers, cleaning mixtures, and inadequately rinsed apparatus.

Because of differences between makes and models of instruments, it is impossible to formulate detailed operating instructions. Follow manufacturer's recommendations for selecting proper photocell and wavelength, adjusting slit width and sensitivity, appropriate fuel and air or oxygen pressures, and the steps for warm-up, correcting for interferences and flame background, rinsing of burner, igniting sample, and measuring emission intensity.

Prepare a blank and sodium or potassium calibration standards in stepped amounts in any of the following applicable ranges: 0 to 1.0, 0 to 10, or 0 to 100 mg/L. Starting with the highest calibration standard and working toward the most dilute, measure emission at 589 nm for sodium and 766 nm for potassium. Repeat the operation with both calibration standards and samples enough times to secure a reliable average reading for each solution. Construct a calibration curve from the calibration standards.

E.5 Quality Control

Quality control (QC) is an integral part of any measurement procedure in order to ensure that results are reliable. A summary of internal QC procedures for each method is given in Table 3-1 and copies of all QC forms are provided in Appendix B. Details on internal QC procedures used in the DDRP are described below.

E.6 Procedure

1. Calibrate the instrument.

2. Analyze samples.

3. Determine concentration of sample from the calibration curve. Where a large number of samples must be run routinely, the calibration curve provides sufficient accuracy. If greater precision and accuracy are desired and time is available, use the bracketing approach described below.

4. Bracketing approach--From the calibration curve, select and prepare standards that immediately bracket the emission intensity of the sample. Determine emission intensities of the bracketing standards (one standard slightly less and the other slightly greater than the sample) and the sample as nearly simultaneously as possible. Repeat the determination on bracketing standards and sample. Calculate the concentration by the equation in Section E.7 and average the findings.

E.7 Calculations

For direct reference to the calibration curve:

$$\text{mg Na}^+ \text{ (or K}^+\text{)/L} = (\text{mg Na}^+ \text{ (or K}^+\text{)/L in portion}) \times D$$

For the bracketing approach:

$$\text{mg Na}^+ \text{ (or K}^+\text{)/L} = \{[(B - A)\,(s - a) \div (b - a)] + A\} \times D$$

where:

B = mg Na$^+$ (or K$^+$)/L in upper bracketing standard,

A = mg Na$^+$ (or K$^+$)/L in lower bracketing standard,

b = emission intensity of upper bracketing standard,

a = emission intensity of lower bracketing standard,

s = emission intensity of sample, and

D = dilution ratio $= \dfrac{\text{mL sample + mL DI water}}{\text{mL sample}}$

E.8 References

American Society for Testing and Materials. 1984. *Annual Book of ASTM Standards, Vol. 11.01, Standard Specification for Reagent Water,* D-1193-77 (reapproved 1983). ASTM, Philadelphia, Pennsylvania.

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